JOURNAL OF THE AMERICAN WATER RESOURCES ASSOCIATION
DECEMBER AMERICAN WATER RESOURCES ASSOCIATION 2004

WATER QUALITY IN AGRICULTURAL, URBAN, AND MIXED LAND USE WATERSHEDS[1]

Chris B. Coulter, Randy K. Kolka, and James A. Thompson[2]

ABSTRACT: Water quality and nonpoint source (NPS) pollution are important issues in many areas of the world, including the Inner Bluegrass Region of Kentucky where urban development is changing formerly rural watersheds into urban and mixed use watersheds. In watersheds where land use is mixed, the relative contributions of NPS pollution from rural and urban land uses can be difficult to separate. To better understand NPS pollution sources in mixed use watersheds, surface water samples were taken at three sites that varied in land use to examine the effect of land use on water quality. Within the group of three watersheds, one was predominately agriculture (Agricultural), one was predominately urban (Urban), and a third had relatively equal representation of both types of land uses (Mixed). Nitrogen (N), phosphorus (P), total suspended solids (TSS), turbidity, pH, temperature, and streamflow were measured for one year. Comparisons are made among watersheds for concentration and fluxes of water quality parameters. Nitrate and orthophosphate concentrations were found to be significantly higher in the Agricultural watershed. Total suspended solids, turbidity, temperature, and pH, were found to be generally higher in the Urban and Mixed watersheds. No differences were found for streamflow (per unit area), total phosphorus, and ammonium concentrations among watersheds. Fluxes of orthophosphate were greater in the Agricultural watershed that in the Urban watershed while fluxes of TSS were greater in the Mixed watershed when compared to the Agricultural watershed. Fluxes of nitrate, ammonium, and total phosphorus did not vary among watersheds. It is apparent from the data that Agricultural land uses are generally a greater source of nutrients than the Urban land uses while Urban land uses are generally a greater source of suspended sediment.

(KEY TERMS: water quality; nonpoint source pollution; watershed management; urban development; chemical fluxes; rural watersheds; land use effects.)

Coulter, Chris B., Randy K. Kolka, and James A. Thompson, 2004. Water Quality in Agricultural, Urban, and Mixed Land Use Watersheds. Journal of the American Water Resources Association (JAWRA) 40(6):1593-1601.

INTRODUCTION

Like in many growing communities, urban water quality and urban watershed management are increasingly important issues in the Inner Bluegrass Region of Kentucky. From 1990 to 2000, the population of Fayette County grew 15.6 percent (U.S. Census Bureau, 2000), increasing the need for housing and related residential and commercial development. Rural lands that were once managed for agriculture now support urban land uses. Determining the impact of urban development on water quality, most often nitrogen, phosphorus, and sediment, has been examined with some success. One approach to measure the effect of urban development is to compare gradients in land use to water quality (McMahon and Cuffney, 2000). In mixed use watersheds, the percentages of each type of land use (urban/agricultural/forested) become important if they differ in their contribution to NPS pollution. McMahon and Harned (1998), in examining the Albemarle-Pamlico drainage basin in the southeast United States, found that land use influenced concentrations of nitrogen and phosphorus concentrations. They found the highest median total nitrogen concentrations in agricultural and developed basins (2.4 and 1.4 mg/l N respectively). Mean total phosphorus concentration was found to be the highest in the developed basins (0.36 mg/l P), and lowest in the agricultural (0.16 mg/l P) and forested basins (0.12 mg/l P). Basnyat *et al.* (2000) found that watershed characteristics such as land use, land cover, slope gradient, and soil type affect water quality and

[1]Paper No. 03032 of the *Journal of the American Water Resources Association* (JAWRA) (Copyright © 2004). **Discussions are open until June 1, 2005.**

[2]Respectively, Department of Agronomy, University of Kentucky, Lexington, Kentucky; Research Soil Scientist, USDA Forest Service, North Central Research Station, 1831 Highway 169E, Grand Rapids, Minnesota 55744; and Assistant Professor, North Carolina State University, Department of Soil Science, 3403D Williams Hall, Raleigh, North Carolina 27695 (E-Mail/Kolka: rkolka@fs.fed.us).

nutrient concentration by regulating sediment loading in the Gulf of Mexico drainage. Thus, anthropogenic influences and natural characteristics of a watershed should be considered when managing watersheds or examining water quality issues (McMahon and Harned, 1998).

As land use changes from agricultural to urban, the natural soil surface is replaced with impermeable surfaces. Infiltration decreases while runoff and flow increase (Corbett *et al.,* 1997). Tourbier (1994) showed that when land is changed from a natural surface to a surface that is 75 to100 percent paved, runoff increases from 10 percent of total precipitation to 55 percent of total precipitation. Furthermore, in urbanized areas streams are frequently channelized, leading to higher peak flows as well as increased sedimentation and erosion (Ferguson and Deak, 1994). Studies comparing drainage basins with different land uses have determined that developed basins have the highest concentrations of suspended solids (McMahon and Harned, 1998).

Wall *et al.* (1996) determined that suspended solids measurements and total phosphorus were highly correlated in an agricultural watershed in Ontario. In the Inner Bluegrass Region of Kentucky, the soil parent materials are relatively rich in P in the form of apatite $[Ca_{10}(PO_4)_6(OH)_1]$, which may influence concentrations of P in surface water. In agricultural watersheds, other P sources may include fertilizers and animal wastes, as well as mineralization, sedimentation, and atmospheric deposition, though research has found very little P results from atmospheric deposition (West and Feagley, 1995). Johnson *et al.* (1976) determined P loss from a New York watershed that was partially forested and partially agricultural. Forty-five percent of dissolved P was from geochemical processes, 35 percent from point sources, and 20 percent from diffuse agricultural sources. In urban watersheds, fertilizers applied to lawns and golf courses, sewage, sedimentation, and atmospheric deposition are possible P sources. Fisher *et al.* (2000) reported N and P concentrations in the Oconee River, Georgia, being elevated by wastewater from the City of Athens from 0.53 mg/l N to 0.78 mg/l N and 0.048 mg/l P to 0.092 mg/l P. Sharpley *et al.* (1999) found that near stream runoff in Pennsylvania accounted for most of the P exported from the watershed, and that 96 percent of this occurred during storm flow.

Nitrate is a common nutrient found in Kentucky water supplies, and at times can exceed the drinking water standard (Conrad *et al.,* 1999). Nitrate in water supplies is contributed mostly from agricultural runoff and, because of its tendency to leach, is correlated with periods of high runoff (Shamblen and Binder, 1996). Liu *et al.* (2000) and Mattikalli and Richards (1996) found levels of nitrate and total dissolved N increased as the percentage of cropland in a watershed increased. The largest contributors of nitrate are chemical fertilizers, animal waste, and, to a lesser degree, mineralization. Some nitrogen may be contributed by dry deposition (nitrate = 6-7 kg/ha/yr^2, ammonium = 2-3 kg/ha/yr^2), but is negligible compared to inputs from chemical fertilizers, that for some crops can be several hundred kg/ha (West and Feagley, 1995). Clark *et al.* (2000) found in a survey of several undeveloped basins across the United States that the median nitrate concentration was 0.087 mg/l. In urban watersheds potential sources include mineralization, human and animal waste, atmospheric deposition, and chemical fertilizers applied to lawns and golf courses.

Ammonium nitrogen may also be present in varying amounts depending on land use. Clark *et al.* (2000) reported median concentrations of 0.02 mg/l NH_4^+ in several undeveloped basins across the United States. In agricultural areas with operations of high animal densities, land applied or stored waste may substantially increase ammonium concentrations by surface runoff and leaching.

In this study, a unique opportunity existed to examine NPS pollution relative to land use in a developing subbasin (1,060 ha) of the East Hickman Creek watershed of Fayette County, Kentucky. The objective was to determine the effect of land use (urban versus agricultural) on specific water quality parameters including nitrate, ammonium, total phosphorus (total P), orthophosphorus, total suspended solids (TSS), turbidity, pH, temperature, and flow. Based on known sources of NPS and the previous literature it is hypothesized that agricultural land uses will lead to greater nutrient concentrations and fluxes while urban land uses will lead to higher to TSS, turbidity, and flow.

METHODS

Study Area

The study area consists of three small watersheds of unnamed tributaries of East Hickman Creek, located in eastern Fayette County, Kentucky. Largely urban, Fayette County is approximately 716.8 km^2 in size and the East Hickman Creek watershed, located in the eastern part of the county, is 21.89 km^2 in area. The northern part of East Hickman Creek watershed includes three smaller streams that all flow into Jacobson Reservoir (Figure 1). Jacobson Reservoir supplies 25 percent of the drinking water for the City

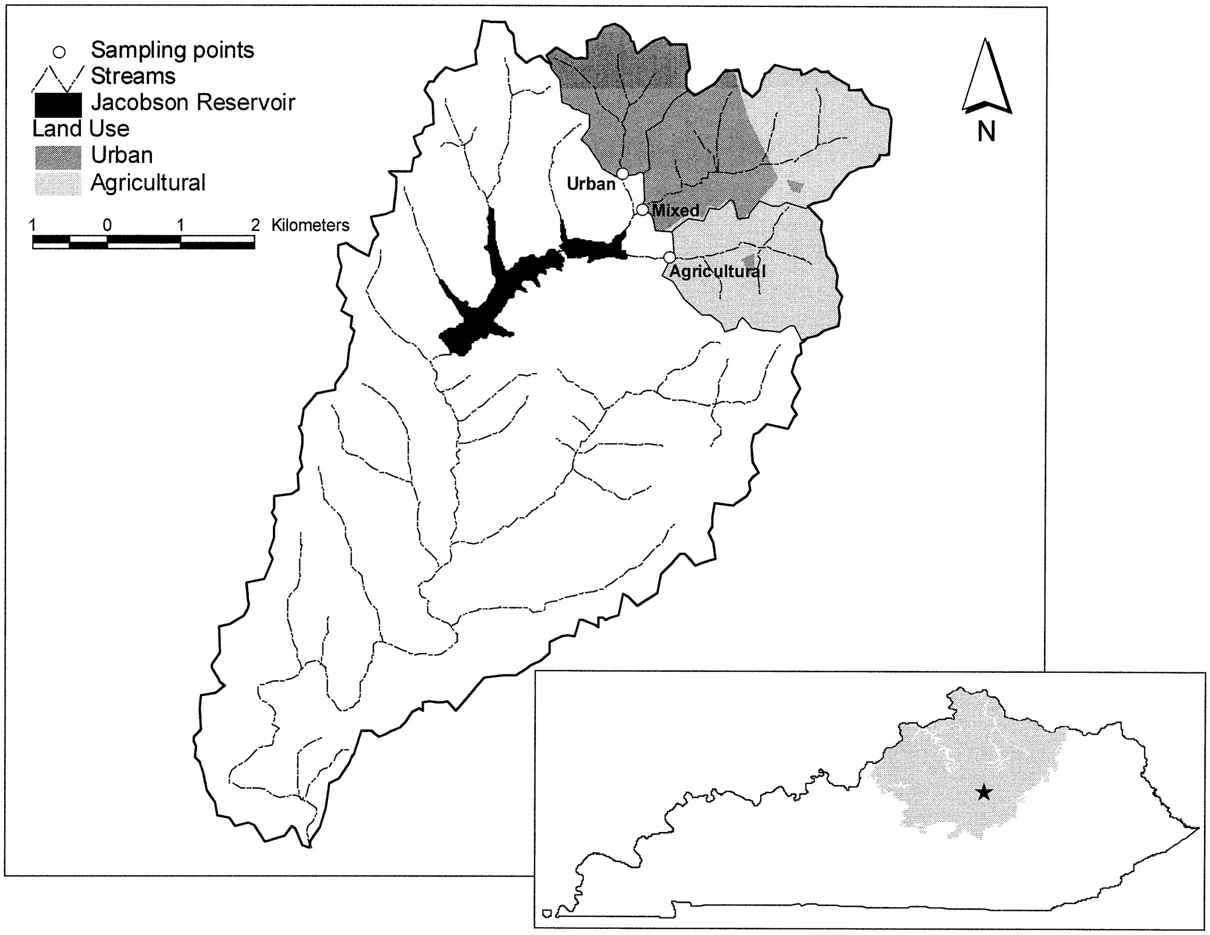

Figure 1. Locations of Stream Water Sampling Points in Three Headwater Watersheds of the East Hickman Creek Watershed. Inset: The location of East Hickman Creek watershed in the Bluegrass Region (shaded) of central Kentucky.

of Lexington, Kentucky (Brion and Lingireddy, 1999). The northern stream flows almost due south through land containing mostly subdivisions of recent development, as well as a golf course, and is largely classified as urban land use (Table 1; Urban Watershed). The southernmost stream drains agricultural land that includes a mix of pasture, cropland, and small woodlots (Table 1; Agricultural Watershed). The eastern stream has headwaters in agricultural land with cropland, woodlots, and some isolated residences in upper watershed and numerous subdivisions and a golf course in lower watershed after it flows under Interstate-75 (Table 1; Mixed Watershed). All three streams are second-order with relatively small flow volumes. Soils in each watershed are dominated by silt loam surface soils and silty clay subsoils with similar taxonomy.

TABLE 1. Land Use Categories for Study Watersheds (Anderson *et al.,* 1976).

Watershed	Percent Agricultural	Percent Urban
Agricultural	95	5
Mixed	43	57
Urban	1	99

Spatial Analysis

Spatial analysis was performed using ArcInfo and ArcView software. Watersheds were delineated and area was calculated for each watershed. Digital land use data was obtained from the Lexington Fayette Urban County Government and updated manually where land use had changed, or where projected land use had not been realized. Land use categories that were classified as urban were retail trade, low, medium, and high density residential, industry, and public recreation areas (Anderson *et al.,* 1976). Land use categories that were classified as agricultural were rural (cropland, pasture, and woodlots) and conservation areas (Anderson *et al.,* 1976).

Stream Water Sampling

Samples were collected on 26 occasions over the period of one year at all three sites, from February 24, 2000, to February 13, 2001. Samples were collected approximately two weeks apart except in April and May when samples were collected weekly. Large rainfall events and the application of fertilizers occur more frequently during this time and the increased sampling intensity provided a more representative record of these events. Sampling was done in both low and high flow periods to better estimate net flux of nutrients and conditions in the streams.

On each of the 26 collection dates, sampling from each of the three sites was completed within two hours. Water samples were collected by hand as grab samples from the middle of the water column. During base flow conditions when water level was low, particular care was used so that stream sediment was not disturbed when samples were taken. The grab samples were collected in polyethylene bottles that had been immersed overnight in 10 percent HCl and rinsed three times with deionized water and again several times with ambient water on site. Two samples were collected from each site. One sample of 1,500 ml was collected to determine total suspended solids and turbidity. A second sample of 25 ml was collected for the analysis of nutrients.

The initial samples collected for nutrient analysis were preserved with 1 N HCL and filtered with 0.45 mm filters in the laboratory, but subsequent samples were filtered with 0.45 mm filters directly in the field, and no acidification was required. Ten ml subsamples for total P were taken prior to filtering. Temperature and pH were recorded in the field using a hand held probe inserted directly into the stream when possible. When conditions did not allow measurement directly from the stream, the measurements were taken from the first grab sample immediately after it was taken. Stage height was recorded at each site during every sample period. Samples were kept cool and transported to the University of Kentucky's Soil and Water Analysis Laboratory within two hours for analysis.

Laboratory Analysis

Nitrate was measured using a modification of the Griess method (Nydahl, 1976). Ten ml of sample and 100 ml of ammonium chloride/ammonium hydroxide buffer solution were reacted with cadmium brushes for 45 minutes and then with N-(1-Naphthyl)-ethylene-diamine dihydrochloride for five minutes. Nitrate concentration was then determined colorimetrically on a Bio-Tek Instruments EL311 colorimeter (Bio-Tek Instruments Inc., Highland Park, Vermont). Ammonium determination was based on the Berthelot reaction and was measured colorimetrically (Chaney and Marbach, 1962).

Total P was determined on unfiltered samples. Ten ml of sample was evaporated overnight to dryness and then 5 ml of 9:1 nitric-perchloric acid was added. After heating overnight, the nitric-perchloric acid was boiled off on a steam plate and the samples were reconstituted with 1 N sulfuric acid to their original volume. Samples were then heated for 20 minutes in closed flasks and allowed to cool. After the digestion, all of the P is converted to PO_4 and the samples were read colorimetrically with the same procedure outlined below for orthophosphate.

Orthophosphate was defined as the phosphorus that passes through a 0.45 mm filter and would react with the molybdonate solution in 10 minutes. Two hundred ml of sample were reacted with 100 ml of 1.75 percent ammonium heptamolybdonate tetrahydrate in 6.3 N sulfuric acid for 10 minutes. Malachite green carbinol hydrochoride dye (100 ml) was then added and allowed to react for 20 minutes before the concentration was read colorimetrically.

For total suspended solids (TSS) a known volume of sample was filtered through oven dried, preweighed 1.2 mm filters (Classer *et al.,* 1989). The filter and retained solids, and filtrate were then dried in a 105˚C oven and weighed.

Streamflow Measurement and Calculation of Fluxes

Streamflow was measured periodically (n = 5 for each site) during the study to develop a rating curve for each stream. Streamflow was measured at different stage heights to assess the range of flow levels. Velocity was measured with a flow meter at multiple locations in the stream (Brooks *et al.,* 1997). A power relationship between flow and stage height was determined at each site and used to estimate flow during each sample period. Stage height flow relationships were all statistically significant at $p \leq 0.10$ (r^2 range from 0.7 to 0.9). Semi-continuous (five-minute interval) stage height data from two U.S. Geological

Survey (USGS) stage height recording stations existed on the Mixed and Agricultural stream. Linear relationships were developed between stage height measured at the USGS stations and that measured at the three sampling points and used to predict mean daily stage height at each of the sample points. A mean daily flow at each sampling point was then estimated using the rating curves. Stage height was measured at all sites on all sample dates except for the Agricultural watershed, which did not have measurable surface flow in August 2000.

Flux for the study period was calculated for nitrate, ammonium, orthophosphate, total P, and TSS. Estimated mean daily flow was multiplied by the known concentrations taken during the 26 sampling events to get a flux of the nutrient for those events. To estimate the concentrations during the periods not sampled, concentration gradients were extrapolated between the measured concentrations. Those estimated concentrations were multiplied by the mean daily flow to estimate the fluxes between sampling periods.

Soil and Streambed Sampling

To characterize nutrient content, streambed sediment at each site and the soils surrounding each site were sampled once and analyzed for pH, total phosphorus, and total nitrogen. Samples were collected in December 2000 and January 2001. The streambed sediment and surface soil samples were both collected as composite samples with a standard 1.9 cm diameter soil probe to a depth of 15 cm. A composite of 12 samples was taken at each site, then air dried, homogenized, and a subsample provided for analysis at the University of Kentucky's Regulatory Services Soil Testing Laboratory.

Statistics

PC-SAS software was used to perform statistical operations. ANOVA analysis and PROC-GLM were used to test for differences in water quality parameters both among watersheds (Agricultural versus Mixed versus Urban). The procedure considers variation over time and unequal sample numbers. To measure seasonal concentration differences, the samples were divided into spring (March, April, May), summer (June, July, August), fall (September, October, November), and winter (December, January, February) periods and compared among watersheds. Six samples were collected each in summer and winter, nine in the spring, and five in the fall. Mean annual nutrient concentrations were calculated by averaging each season and the four seasons were combined to obtain an overall mean concentration for the year. Differences between average annual concentrations, temperature, flow, and flux of nutrients were determined using paired t-tests. A significance level of 90 percent ($p \leq 0.10$) was used for both ANOVA and t-tests unless otherwise noted.

RESULTS AND DISCUSSION

Watershed Land Use and Streamflow

Land use within each watershed was classified as being either agricultural or urban based on the Anderson land use classification scheme (Table 1) (Anderson *et al.,* 1976). The Agricultural watershed was 327 ha in size and 95 percent agricultural (Figure 1). The Mixed watershed was 506 ha in size and was 57 percent urban and 43 percent agricultural. The Urban watershed was 226 ha and was 99 percent urban. The delineation of land uses in the watershed indicated that land uses do vary considerably among the three sites.

An effect on streamflow per unit area was expected given the perceived differences in impervious surface between the urban and agricultural watersheds. Although mean annual streamflow varied among watersheds (data not shown), streamflow per unit area was similar among sites (Table 2). Unlike other studies that have found increases in runoff and streamflow resulting from urbanization (Tourbier, 1994), this study did not. The development in the Urban and Mixed watersheds in this study is mainly residential with golf courses located in both watersheds. Based on the results contained herein it appears that the amount of impervious surface resulting from residential and golf course development does not markedly affect watershed level infiltration.

Nitrogen

The Agricultural watershed had a significantly higher mean nitrate concentration during the study period than the Mixed and Urban watersheds and the Mixed watershed had significantly higher nitrate concentrations than the Urban watershed (Table 2). The highest concentration during the study period (5.96 mg/l) was recorded in the Agricultural watershed. A mean nitrate concentration of 0.09 mg/l has been reported for undeveloped stream basins in the Eastern U.S. by Clark *et al.* (2000). Compared with undeveloped basins, the nitrate in surface water in

TABLE 2. Mean Concentrations of Nitrate, Ammonium, Orthophosphate, and Total Phosphorus, Temperature, pH, Turbidity, and Flow for the Sample Year.

	NO_3 (mg/l)	NH_4 (mg/l)	PO_4 (mg/l	TP (mg/l)	Temp (˚C)	pH	Turbidity (mg/l)	TSS (mg/l)	Flow L/s ha^2
Agricultural	**1.57a**	**0.14a**	**0.05a**	**0.44 a**	**15.1 a**	**7.25 a**	**14.8 a**	**13.3 a**	**0.086 a**
Spring	1.57 a		0.05 a	0.61 a	15.9 a	7.27 a	14.7 a	13.4 a	
Summer	0.32 b		0.08 a	0.51 ab	23.1 b	7.35 a	19.1 a	17.6 a	
Fall	0.51 b		0.05 a	0.40 b	15.4 a	7.06 b	11.0 a	8.8 a	
Winter	3.30 c		0.03 a	0.17 c	7.0 c	7.25 a	13.8 a	12.4 a	
Mixed	**0.78 b**	**0.23 a**	**0.02 b**	**0.41 a**	**17.4 b**	**7.32 a**	**23.4 b**	**23.1 b**	**0.091 a**
Spring	0.60 a		0.03 a	0.49 a	18.6 a	7.39 a	37.4 a	37.8 a	
Summer	0.42 a		0.03 a	0.51 a	26.0 b	7.21 b	12.2 b	8.8b	
Fall	0.32 a		0.01 a	0.40 a	16.8 a	7.30 ab	12.0 b	11.1 ab	
Winter	1.79 b		0.01 a	0.27 a	7.4 c	7.34 a	23.3 ab	25.6 ab	
Urban	**0.52 c**	**0.35 b**	**0.02 b**	**0.34 a**	**17.3 b**	**7.46 b**	**21.7 ab**	**20.8 ab**	**0.078 a**
Spring	0.41 a		0.03 a	0.28 a	18.9 a	7.56 a	21.3 ab	21.6 a	
Summer	0.15 a		0.01 a	0.63 b	27.6 b	7.51 a	14.3 b	10.0 a	
Fall	0.18 a		0.02 a	0.30 a	15.6 a	7.27 b	8.0 c	5.8 a	
Winter	1.35 b		0.01 a	0.16 a	6.0 c	7.49 a	41.0 a	40.4 a	

Note: Different letters mean significant difference at $p = 0.10$, seasonal differences within site only

study watersheds is apparently influenced by human activities. Seasonal differences existed for nitrate concentration across all watersheds with concentrations in winter months being highest (Table 2). Nitrate concentration was significantly correlated ($r^2 > 0.68$ at all sites) with stage height and the highest stage heights occurred during January and February (data not shown). The higher percentage of cropland in the Agricultural watershed may have resulted in the higher nitrate concentrations. During the study period, corn and burley tobacco crops were present in the rural watersheds, both of which require heavy application of nitrogen fertilizers.

The flux of nitrate was not significantly different among watersheds although trends are apparent with the flux from the Agricultural watershed noticeably greater than either the Mixed or the Urban watershed (Table 3). The lowest annual flux of nitrate was from the Urban site, which also had the lowest percentage of agricultural land in the watershed. Results for all three watersheds were high compared to four agricultural watersheds monitored in Iowa for six years where nitrate flux averaged 3.68 kg/ha (Burwell *et al.,* 1977).

The highest mean concentration of ammonium for the year (0.35 mg/l) was at the Urban site although there was no significant difference among mean values at the three sites (Table 2). Ammonium concentrations were higher than a mean concentration of 0.02 mg/l reported in undeveloped basins by Clark *et al.* (2000). The higher concentration in the Urban watershed could have been due to the high ammonium waste of a resident waterfowl population present on a golf course near the Urban sample site. Highest annual flux of ammonium (0.95 kg/ha) occurred in the Mixed watershed, but ammonium flux was also not significantly different among sites (Table 3). Ammonium flux at the sites in this study was similar to that reported by Burwell *et al.* (1977) in four agricultural watersheds in Iowa (0.17 to 0.64 kg/ha NH_4^+).

Soil and sediment analysis for total nitrogen indicated higher concentrations of nitrogen in both sediment and soils at the Agricultural site and may explain the higher nitrate concentrations in the stream water of the Agricultural watershed (Table 4).

Phosphorus

Mean annual total P concentrations were not different among watersheds (Table 2), nor were fluxes of total P (Table 3). Total P concentration changed by season at every site except at the Mixed site. In the Urban watershed, total P concentration was highest in the summer months and lowest in the winter. In the Agricultural watershed total P was highest in the spring, and lowest in the winter. The total P fluxes are somewhat higher than annual total P fluxes reported by Burwell *et al.* (1977) of 0.58 kg/ha for agricultural watersheds.

TABLE 3. Annual and Seasonal Chemical and Suspended Flux at Each Site.

	NO_3^- (mg/l)	NH_4 (mg/l)	PO_4 (mg/l	Total P (mg/l)	TSS (mg/l)
Agricultural	**20.4 a**	**0.34 a**	**0.28 a**	**1.13 a**	**93.6 a**
Spring	1.85	0.05	0.18	0.36	8.32
Summer	0.00	0.00	0.04	0.00	0.04
Fall	0.41	0.12	0.03	0.19	5.55
Winter	18.1	0.18	0.02	0.57	79.7
Mixed	**10.8 a**	**0.95 a**	**0.12 ab**	**1.14 a**	**160.0 b**
Spring	6.62	0.78	0.08	0.63	78.8
Summer	0.08	0.03	0.01	0.06	2.09
Fall	0.19	0.08	0.01	0.22	5.78
Winter	3.93	0.06	0.02	0.24	73.4
Urban	**5.97 a**	**0.52 a**	**0.07 b**	**0.66 a**	**107.4 ab**
Spring	3.98	0.12	0.06	0.24	74.7
Summer	0.02	0.00	0.00	0.08	1.62
Fall	0.14	0.14	0.01	0.19	2.60
Winter	1.84	0.26	0.01	0.14	28.5

Note: Different letters mean significant difference at $p = 0.10$.

Mean orthophosphate concentrations were significantly higher in the Agricultural watershed than in the Mixed and Urban watersheds (Table 2). The mean annual orthophosphate concentrations in this study are slightly less than the 0.08 mg/l PO_4 reported by Johnson *et al.* (1976) for orthophosphate in surface runoff of unmanured cropland. The mean annual and seasonal orthophosphate concentrations in the Agricultural watershed equaled or exceeded the 0.03 mg/l limits likely to cause eutrophication (Stevens *et al.,* 1999), but were subject to fluctuation above and below the limit throughout the sample period. Orthophosphate was not correlated with flow, which corresponds to the results of Johnson et al. (1976). No differences existed for seasonal concentrations of orthophosphate within individual sites (Table 2).

Annual flux of orthophosphate was highest for the Agricultural watershed, which was significantly higher than the lowest annual flux, which occurred at the Urban watershed (Table 3). Burwell *et al.* (1977) reports an annual mean flux of soluble P from agricultural watersheds of 0.13 kg/ha, which is similar to levels found in the study watersheds. Orthophosphate flux was highest in the spring for all watersheds. Seasonal differences appear to be the result of higher flow in the spring and not a fertilizer effect. Orthophosphate flux could be expected to change substantially annually based on inputs of P in the watershed and amount of P stored in the streambed (Johnson *et al.,* 1976).

Soil and sediment analysis for total P indicated higher concentrations of phosphorus in both sediment and soils at the Agricultural site (Table 4). Phosphorus enriched sediment derived from nearby soils result in accumulated bed sediment that is high in accumulated P (Huanxin *et al.,* 1997). Although the bed sediment could either be a source or a sink of phosphorus, in this study it appears to be a source because of the higher dissolved P concentrations and fluxes in the Agricultural watershed (Tables 2 and 3).

TABLE 4. Streambed Sediment and Soil Chemistry for Rural, Mixed, and Urban Land Uses.

Matrix/Land Use	Total N (mg/kg)	Total P (mg/kg)	pH
Sediment			
Agricultural	4,090	147	7.5
Mixed	2,562	48	7.3
Urban	3,022	36	7.1
Soil			
Agricultural	4,809	163	7.2
Mixed	3,011	78	7.6
Urban	3,882	89	7.4

Total Suspended Solids and Turbidity

Mean annual TSS and turbidity concentrations were significantly different among sites with higher TSS and turbidity in the Mixed watershed than in the

Agricultural watershed (Table 2). Concentrations in the Urban watershed were similar to the Mixed watershed but were not different than Agricultural watershed at the $p \leq 0.10$ significance level. Differences in TSS and turbidity concentrations did exist between Urban and Agricultural watersheds at the $p = 0.25$ significance level. Most of the annual TSS and turbidity was associated with periods of high flow and tended to peak with precipitation events. There was also a difference in TSS and turbidity concentrations among season in the Urban and Mixed watersheds but not in the Agricultural watershed. In the Urban and Mixed watersheds, TSS and turbidity concentrations were highest in the winter and spring and lowest in the summer and fall. The seasonal differences present in the Urban and Mixed watersheds are likely related to ongoing construction and soil disturbance occurring in the watersheds during winter and spring when cover crops are difficult to establish. The highest annual flux of TSS was from the Mixed watershed which was significantly higher than the Agricultural watershed, with the Urban watershed not different from either the Mixed or Agricultural watershed (Table 3). Again, construction and the associated soil disturbance in the Mixed watershed likely led to higher TSS and turbidity.

Turbidity and TSS concentrations were highly correlated at all sites, explaining 88 to 99 percent of the variability. Thus turbidity measurements could reasonably be used to predict concentrations of TSS. In this study there was little correlation between TSS or turbidity and total P concentrations, making prediction of total P from TSS or turbidity inaccurate in these watersheds.

Temperature and pH

Stream water temperature was significantly higher in the Urban and Mixed watersheds than in the Agricultural watershed (Table 2). Although percent cover was not measured, direct observations of the riparian areas in the Agricultural watershed indicate more tree cover than in the Urban or Mixed watershed. The shading likely led to the temperature differences among the watersheds. The highest temperature range was recorded at the Urban site (1.1 to 32.0°C), the lowest at the Agricultural site (4.0 to 24.1°C). A large temperature range supports the possible lack of buffering in the less shaded urban areas. Not surprisingly, seasonal differences existed for temperature at all sites with temperature being highest in summer and lowest in winter.

In the Urban watershed pH was significantly higher than in either Mixed or Agricultural watersheds (Table 2). At all sites the pH was basic, and can be attributed to the limestone derived soils and calcareous ground water in the watersheds. The significantly lower pH of the Agricultural stream could be a result of interflow through slightly lower pH soils found in the Agricultural watershed (Table 4). In the Agricultural and Urban watersheds there was a seasonal change in pH, with pH being significantly lower in the fall (Table 2). In the Mixed watershed, pH was significantly lower during the summer.

CONCLUSION

All watersheds in this study appear to be impacted to various extents by NPS pollution coming from urban and agricultural land uses. Factors such as type of disturbance, length of disturbance, proximity to stream, watershed size, and vegetation may play complex roles that this study did not take into account. Some differences in water quality parameters appeared to be clearly related to land use. In the future, as the percentage of developed land in the watersheds increases, more substantial impacts should be observable.

Nitrate and orthophosphate stream concentrations were higher in the Agricultural watershed and TSS, turbidity, temperature, and pH were higher in the stream draining the Urban watershed. Total phosphorus and ammonium concentrations and flow per unit area did not vary by watershed. For most water quality variables the Mixed watershed concentrations either fell between those for the Agricultural and Urban watersheds (e.g., nitrate) or were more closely related to the Urban watershed concentrations (e.g., orthophosphate, TSS, turbidity, and temperature). For most water quality parameters the Mixed watershed tended to be more similar to the Urban watershed, likely as a result of the nearness to urban sources as compared to nearness of agricultural sources (Figure 1). Although a considerable area of the watershed was agricultural the area near the sampling location was predominantly urban.

Higher nitrate and orthophosphate concentrations in the Agricultural stream were likely caused by higher areal rates of fertilization during cropping. Higher TSS and turbidity concentrations and higher temperature in the Urban and Mixed streams are likely the result of poorer management of the riparian zones when compared to Agricultural streams, as well as ongoing development and associated soil disturbance.

Fluxes of nutrients and sediment varied considerably among sites and land uses because of their dependence on flow. Fluxes of nitrate, ammonium and total P did not vary by site although a trend is apparent for nitrate with the Agricultural watershed having the greatest flux, followed by the Mixed and Urban Watersheds. Orthophosphate flux was highest in the Agricultural watershed while TSS was highest in the Mixed watershed. As for concentrations, it is apparent that the Agricultural land uses are greater sources of nutrients while Urban land uses are greater sources of sediment.

Quantifying water quality can be difficult because of the dynamic and seasonal influences of small watersheds and depends on natural as well as anthropogenic factors. The results of this study show that land use can be an important influence on water quality. The variability that exists suggests that study of watersheds on this scale will continue to be important, especially in areas where land use is mixed and/or changing.

LITERATURE CITED

Anderson, J.R., E.E. Hardy, J.T. Roach, and R.E. Witmer, 1976. A Land Use and Land Cover Classification System for Use With Remote Sensor Data. U.S. Government Printing Office, Washington D.C. Geological Survey Professional Paper 964.

Basnyat, P., L.D. Teeter, B.G. Lockaby, and K.M. Flynn, 2000. The Use of Remote Sensing and GIS in Watershed Level Analyses of Non-Point Source Pollution Problems. For. Ecol. Manage. 128: 65-73.

Brion, G.M. and S. Lingireddy, 1999. A Neural Network Approach to Identifying Non-Point Sources of Microbial Contamination. Water Res. 33:3099-3106.

Brooks, K.N., P.F. Ffolliott, H.M. Gregersen, and L.F. DeBano, 1997. Hydrology and the Management of Watersheds (Second Edition). Iowa State University Press, Ames, Iowa, pp. 139-163.

Burwell, R.E., G.E. Schuman, H.G. Heinemann, and R.G. Spomer, 1977. Nitrogen and Phosphorus Movement From Agricultural Watersheds. J. Soil Water Cons. 32: 226-230.

Chaney, A.L. and E.P. Marbach, 1962. Modified Reagents for Determination of Urea and Ammonia. Clin. Chem. 8:130-132.

Clark, G. M., D. K. Mueller, and M. A. Mast. 2000. Nutrient Concentrations and Yields in Undeveloped Stream Basins of the United States. J. A. W. Res. Assoc. 36: 849-860.

Classer, L.S., A.E. Greenburg, and R.R. Trussell (Editors), 1989. Standard Methods for the Examination of Water and Wastewater (17th Edition). Port City Press, Baltimore, Maryland, pp. 2.75-2.77.

Conrad, P.G., D.I. Carey, J.S. Webb, J.S. Dinger, and M.J. McCourt, 1999. Ground-Water Quality in Kentucky: Nitrate-Nitrogen. Kentucky Geological Survey Information Circular 60, Series XI.

Corbett, C.W., M. Wahl, D.E. Porter, D. Edwards, and C. Moise, 1997. Nonpoint Source of Runoff Modeling: A Comparison of a Forested Watershed and an Urban Watershed on the South Carolina Coast. J. Exp. Marine Biol. Ecol. 213:133-149.

Ferguson, B.K. and T. Deak, 1994. Role of Urban Storm-Flow Volume in Local Drainage Problems. J. Water Res. Planning and Mgt. 120:523-530.

Fisher, D.S., J.L. Steiner, D.M. Endale, J.A. Stuedemann, H.H. Schomberg, A.J. Franzluebbers, and S.R. Wilkinson, 2000. The Relationship of Land Use Practices to Surface Water Quality in the Upper Oconee Watershed of Georgia. For. Ecol. Manage. 128:39-48.

Huanxin W., B.J. Presley, and D.J. Velinsky, 1997. Distribution and Sources of Phosphorus in Tidal River Sediments in the Washington, D.C., Area. Env. Geol. 30: 224-230.

Johnson, A.H., D.R. Bouldin, E.A. Goyette, and A.M. Hedges, 1976. Phosphorus Loss by Stream Transport From a Rural Watershed: Quantities, Processes, and Sources. J. Env. Qual. 5:148-157.

Liu, Z., D.E. Weller, D.L. Correll, and T.E. Jordan, 2000. Effects of Land Cover and Geology on Stream Chemistry in Watersheds of Chesapeake Bay. Journal of the American Water Resources Association (JAWRA) 36(6):1349-1365.

Mattikalli, N.M. and K.S. Richards, 1996. Estimation of Surface Water Quality Changes in Response to Land Use Change: Application of the Export Coefficient Model Using Remote Sensing and Geographical Information System. J. Env. Mgt. 48:263-282.

McMahon, G. and D.A. Harned, 1998. Effect of Environmental Setting on Sediment, Nitrogen, and Phosphorus Concentrations in Albemarle-Pamlico Drainage Basin, North Carolina and Virginia, USA. Env. Manage. 22:887-903.

McMahon, G. and T.F. Cuffney, 2000. Quantifying Urban Intensity in Drainage Basins for Assessing Stream Ecological Conditions. Journal of the American Water Resources Association (JAWRA) 36(6):1247-1261.

Nydahl, F., 1976. On the Optimum Conditions for the Reduction of Nitrate by Cadmium. Talanta 23:349.

Shamblen, R.G. and D.M. Binder, 1996. The Effect of Watershed, Reservoir Volume, and Rainfall on Nitrate Levels in Surface Drinking Water Supplies. J. of Soil and Water Cons. 51:457-462.

Sharpley, A.N., W.J. Gburek, G. Folmar, and H.B. Pionke, 1999. Sources of Phosphorus Exported From an Agricultural Watershed in Pennsylvania. Ag. Water Manage. 41:77-89.

Stevens, D.P., J.W. Cox, and D.J. Chittleborough, 1999. Pathways of Phosphorus, Nitrogen, and Carbon Movement Over and Through Texturally Differentiated Soils, South Australia. Australian J. Soil Res. 37:679-694.

Tourbier, J.T., 1994. Open Space Through Stormwater Management: Helping to Structure Growth on the Urban Fringe. J. Soil Water Cons. 49:14-22.

U.S. Census Bureau, 2000. (CO-99-6) Numeric and Percent Population Change for Counties: Within-State and National Rankings, April 1, 1990, to July 1, 1999 (CO-99-6). *Available at* <www.census.gov/population/estimates/county/co-99-6/99C6_21.txt>. *Accessed on* September 10, 2001.

Wall, G.J., A.W. Bos, and A.H. Marshall, 1996. The Relationship Between Phosphorus and Suspended Sediment Loads in Ontario Watersheds. J. Soil Water Cons. 51:504-507.

West, L.M. and S.E. Feagley, 1995. The Chemical Composition of Atmospheric Deposition Collected From Six Louisiana Sites From 1983 to 1992. Atms. Env. 29: 1211-1217.