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Dissolved and particulate nutrient flux from three adjacent agricultural watersheds: A five-year study

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Abstract. Fluxes of dissolved and particulate nitrogen (N) and phosphorus (P) from three adjacent watersheds were quantified with a high-resolution sampling program over a five-year period. The watersheds vary by an order of magnitude in area (12,875, 7968 and 1206 ha), and in all three watersheds intensive agriculture comprises > 90% of land. Annual fluxes of dissolved N and P per unit watershed area (export coefficients) varied ~2X among watersheds, and patterns were not directly related to watershed size. Over the five-year period, mean annual flux of soluble reactive P (SRP) was 0.583 kg P $\cdot$ ha^{-1} $\cdot$ yr^{-1} from the smallest watershed and 0.295 kg P $\cdot$ ha^{-1}$\cdot$ yr^{-1} from the intermediate-sized watershed, which had the lowest SRP flux. Mean annual flux of nitrate was 20.53 kg N $\cdot$ ha^{-1} $\cdot$ yr^{-1} in the smallest watershed and 44.77 kg N $\cdot$ ha^{-1} $\cdot$ yr^{-1} in the intermediate-sized watershed, which had the highest nitrate flux. As a consequence, the export ratio of dissolved inorganic N to SRP varied from 80 (molar) in the smallest watershed to 335 in the intermediate-sized watershed. Because most N was exported as nitrate, differences among watersheds in total N flux were similar to those for nitrate. Hence, the total N:P export ratio was 42 (molar) for the smallest watershed and 109 for the intermediate-sized watershed. In contrast, there were no clear differences among watersheds in the export coefficients of particulate N, P, or carbon, even though > 50% of total P was exported as particulate P in all watersheds. All nutrient fractions were exported at higher rates in wet years than in dry years, but precipitation-driven variability in export coefficients was greater for particulate fractions than for dissolved fractions.

Examination of hydrological regimes showed that, for all nutrient fractions, most export occurred during stormflow. However, the proportion of nitrate flux exported as baseflow was much greater than the proportion of SRP flux exported as baseflow, for all three watersheds (25–37% of nitrate exported as baseflow vs. 3–13% of SRP exported as baseflow). In addition, baseflow comprised a greater proportion of total discharge in the intermediate-sized watershed (43.7% of total discharge) than the other two watersheds (29.3 and 30.1%). Thus, higher nitrate export coefficients in the intermediate-sized watershed may have resulted from the greater contribution of baseflow in this watershed. Other factors potentially contributing to higher

nitrate export coefficients in this watershed may be a thicker layer of loess soils and a lower proportion of riparian forest than the other watersheds. The among-watershed variability in SRP concentrations and export coefficients remains largely unexplained, and might represent the minimum expected variation among similar agricultural watersheds.

Introduction

The quantities of nutrients exported from watersheds to surface waters affect aquatic productivity, food web structure and water quality, and can provide much information about the characteristics of the contributing terrestrial landscape (Allan et al. 1997; Caraco & Cole 1999; Carpenter et al. 1998; Dillon & Kirchner 1975; Howarth et al. 1996; Likens & Bormann 1995; Vitousek et al. 1979). It is well known that nutrient flux from watersheds is affected by geology, topography and climate, as well as human activities. Nutrient fluxes from watersheds with a preponderance of agricultural lands can be orders of magnitude higher than that from undisturbed forests (Beaulac & Reckhow 1982; Cleresci et al. 1986; Logan 1990; Mueller et al. 1995; Puckett 1995; Smith et al. 1987). Indeed, non-point runoff of nitrogen (N) and phosphorus (P) from agricultural landscapes is viewed as one of the most important factors causing impaired water quality in freshwater and estuarine ecosystems (Correll 1998; Carpenter et al. 1998; Daniel et al. 1998; Downing et al. 1999; Hessen et al. 1997; Howarth 1988; Puckett 1995; Sims et al. 1998; Smith et al. 1987).

Despite the general trend of higher nutrient exports from disturbed watersheds, it remains difficult to predict flux rates even if land use patterns are well-characterized (e.g. Mueller et al. 1995; Puckett 1995). For example, relationships between land use factors (e.g. percent of agricultural, urban or forested land) and nutrient flux (or water quality) are highly variable (Hunsaker & Levine 1995; Jordan et al. 1997a; Mueller et al. 1995; Omernik 1976; Osborne & Kovacic 1993; Soranno et al. 1996). Furthermore, watersheds with similar land use can vary greatly with respect to nutrient fluxes or in-stream concentrations (Dillon & Kirchner 1975; Clesceri et al. 1986; Mueller et al. 1995; Puckett 1995).

Several factors can potentially account for variation in nutrient flux rates from watersheds of similar land use. Watershed area may affect fluxes. Some studies show that smaller watersheds have higher specific fluxes (i.e. flux per unit area) than larger watersheds (Prairie & Kalff 1986; Soranno et al. 1996). However, others show no effect of watershed size on flux rates (Boggess et al. 1995). Spatial patterns within a landscape, such as the location of agricultural fields relative to streams, the proportions of watershed areas which are sources or sinks for nutrients, and the distribution and extent of riparian buffers, can affect watershed-scale nutrient exports (Creed & Band 1998; Gburek & Sharpley 1998; Hill 1996; Hunsaker & Levine 1995; Jordan et al 1993; Sharpley 1995; Soranno et al. 1996). Soil characteristics can also mediate the relationship between overall land use and nutrient export (Dillon & Kirchner 1975; Heckrath et al. 1995; Kalhkoff 1995; Steinheimer et al. 1998).

Some of the observed variability in nutrient fluxes may derive from variable sampling regimes. Nutrient fluxes can show tremendous temporal variation, corresponding to precipitation-mediated variation in stream discharge. These fluxes can be accurately characterized only through very intensive sampling (Baker 1993; Richards & Baker 1993; Steinheimer et al. 1998). Often, sampling regimes are not designed to adequately capture this variation, potentially leading to biased estimates of fluxes (e.g. Cohn et al. 1989; Richards & Holloway 1987). This may be particularly true in agricultural watersheds, where both concentrations and discharge increase dramatically during storms, leading to enormous temporal variation in nutrient fluxes over short time scales (days or even hours; e.g. Baker 1993; Steinheimer et al. 1998). Finally, flux rates of different elements (e.g. N vs. P) and nutrient fractions (e.g. solutes vs. particulates) may show different temporal patterns and annual fluxes. Surprisingly few studies have quantified fluxes of all fractions of particulate and dissolved nitrogen and phosphorus from watersheds, and there is considerable variation among studies in which fractions are quantified. This renders comparisons among watersheds difficult. Therefore, accurate estimates of dissolved and particulate N and P fluxes, obtained from adequately designed sampling regimes, are needed.

Our objective in this study was to quantify nutrient concentrations and fluxes from three adjacent agricultural watersheds that are very similar in land use and physical factors but vary in area. We employed an intensive, stratified sampling regime in which both particulate and dissolved fractions of N and P were quantified over a 5-year period, during which annual precipitation varied considerably. We are thus able to effectively test the null hypothesis that N and P export flux rates are similar among watersheds of similar land use.

Study sites

We quantified nutrient concentrations and fluxes in three watersheds within the Upper Four Mile Creek (UFMC) watershed in southwestern Ohio and southeastern Indiana, USA (Figure 1). Agricultural land (cropland and pastureland) comprises more than 90% of our study watersheds (Table 1).

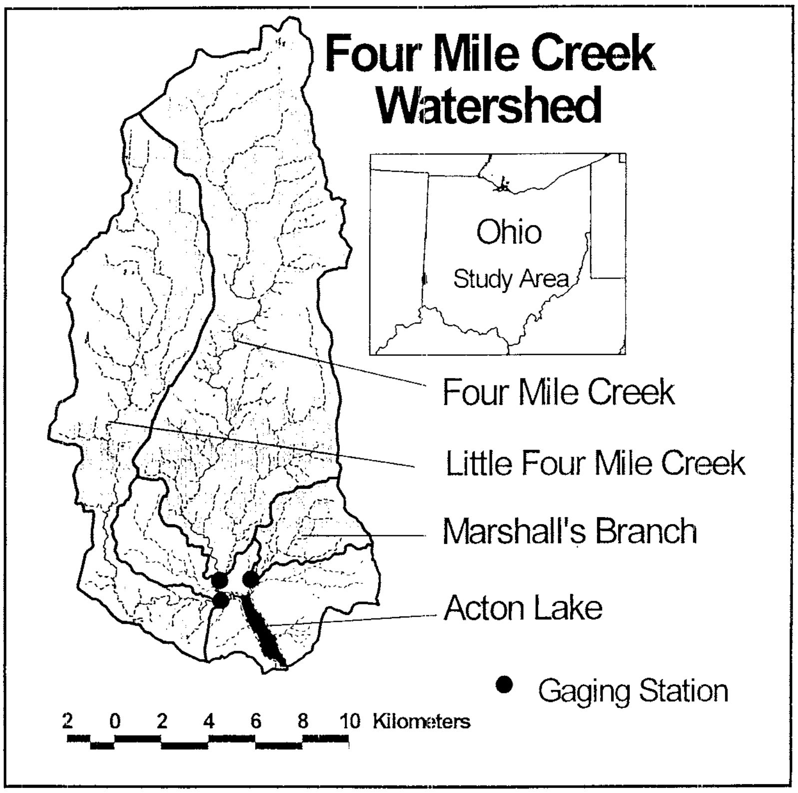

Figure 1. Map of the Upper Four Mile Creek Watershed showing boundaries of the three study watersheds (shaded) and locations of stream gaging stations.

Between 1994 and 1998 (the years of this study), croplands in the study area consisted mostly of corn or soybean, and conservation tillage was commonly practiced on corn and soybean fields (Table 2). The watershed drains into Acton Lake, a eutrophic reservoir that typically exhibits poor water quality including elevated nutrient concentrations, inorganic turbidity and phytoplankton biomass, and low water clarity (Schaus et al. 1997; Winner et al. 1962). The lake is categorized as impacted by non-point sources (USDA 1992).

The three watersheds we studied vary in size by an order of magnitude and together comprise 86% of the Upper Four Mile Creek Watershed. Four Mile Creek (12,875 ha) and Marshall's Branch (1,206 ha) drain 50% and 5% of the UFMC watershed, respectively, and are located entirely within Preble County, Ohio. Little Four Mile Creek (7,968 ha) drains 31% of the UFMC watershed in Preble County, and Union and Wayne counties in Indiana (Figure 1). Land use is very similar among the three watersheds and is reflective of the entire

Table 1. Watershed area and land use. Data are derived from Ohio Department of Natural Resources from 1994

Watershed	Area (ha)	Land use (percent of watershed area)			
		Agriculture	Forest	Urban	Other
Four Mile Creek	12875	91.2	8.0	0.5	0.3
Little Four Mile Creek	7968	94.1	4.9	0.7	0.4
Marshall's Branch	1206	91.7	7.3	0.7	0.3

Table 2. Cropland use and tillage data. Data were provided by Preble, Wayne and Union County Soil Conservation District offices. The "Upper Four Mile Creek (UFMC) within Preble County" data include areas from all three watersheds within Preble County; data are not available separately for each watershed. Wayne and Union County data are county-wide, but are assumed to reflect landuse and tillage in our study watersheds. Cropland is classified as conservation tillage if > 30% of surface residue cover is maintained after planting, following Natural Resource Conservation District definitions

Land unit	Percent of Upper Four Mile Creek Watershed located in land unit	Percent of cropland		Percent of corn and soybean crops in conservation tillage
		Corn	Soybeans	
[1]UFMC within Preble County	82.5	48.7	41.2	48.8
[2]Union County	16.0	41.8	33.1	39.6
[3]Wayne County	1.5	47.2	43.2	57.5

[1]Mean from 1994, 1995, 1996 and 1998; [2]Mean from 1996–1998; [3] Mean from 1994–1998

UFMC watershed (Table 1). Soils are of high-lime glacial till capped with highly productive silt loess (Medley et al. 1995; USDA 1992). The Little Four Mile Creek watershed consists of Ragsdale, Reesville and Birkbeck soils (in northern areas) or Russell, Xenia and Fincastle soils (in southern areas), with a relatively thick (up to 150 cm) loess layer (USDA 1992). The loess layer is thinner in the Four Mile Creek and Marshall's Branch watersheds, and Crosby, Brookston, Miami and Celina soils dominate. Ross, Medway and Fox soils are present in valleys and adjacent to streams.

Methods

Sampling and analytical methods

We quantified discharge, nutrient concentrations and nutrient fluxes using gaging stations installed on each of the three streams just upstream of where they enter Acton Lake (Figure 1). Gaging stations were installed on Four Mile Creek in 1992, on Marshall's Branch in 1993 and on Little Four Mile Creek in May 1994. Here we report nutrient dynamics for five full years, from 1994 through 1998.

Stage was recorded at each gaging station at 10-minute intervals using pressure transducers installed in stilling wells, connected to Campbell dataloggers. Stage was converted to discharge with standard rating-curve techniques using field discharge measurements (Kennedy 1983). On rare occasions (< 10% of possible data points) one of the dataloggers failed to record data due to battery depletion or other technical problem. Under these circumstances discharge was estimated using regressions of discharge at that station vs. discharge at one of the other stations. Water samples for nutrient analyses were collected using ISCO programmable pumping samplers. We employed a stratified sampling regime with more frequent sampling during storms than during baseflow, generally following sampling protocols established for other studies in agricultural watersheds in Ohio (Baker 1993; Richards & Baker 1993). Thus, during storms samples were collected at 2–6 hr intervals. From 1994 through 1996 baseflow samples were collected irregularly while in 1997 and 1998 baseflow samples were collected daily.

Our goal was to characterize fluxes of dissolved, particulate and total N and P. Therefore we quantified various fractions of these elements, although not all fractions were quantified in all years. We analyzed samples for ammonium-N (NH_4-N), nitrate & nitrite-N (NO_3-N), and soluble reactive P (SRP) over all years of the study period on > 4000 samples (at least 1200 samples per stream). We also quantified total dissolved N (TDN) and total dissolved P (TDP) in 1997–1998 (> 1500 samples); particulate phosphorus in 1995–1997 (> 3500 samples); particulate carbon and particulate nitrogen in 1995–1996 (> 2400 samples) and suspended solids (SS) in 1995–1998 (> 4000 samples).

Dissolved nutrients (NO_3-N, NH_4-N, SRP, TDN and TDP) were analyzed on samples passed through Gelman AE glass fiber filters (1.0 μm nominal pore size). SRP was analyzed manually with the molybdenum blue technique (Murphy & Riley 1962); TDP was analyzed in the same manner except that samples were first digested with potassium persulfate. Dissolved NH_4-N was analyzed manually with the phenolhypochlorite technique (Solarzano 1969). NO_3-N and TDN were quantified with second derivative spectrophotometry (Crumpton et al. 1992) on undigested samples (NO_3-N) or on samples digested with low-N potassium persulfate (TDN). Particulate C, N and P concentrations were assayed by filtering stream water onto pre-ashed Gelman AE glass-fiber filters and analyzing filters for nutrient contents. Particulate C and N were analyzed with a Perkin Elmer Series 2400 CHN analyzer. The particulate C concentrations we present here include organic and inorganic C; analysis of samples with and without ashing revealed that organic C usually comprised > 95% of particulate C. Particulate P was assayed with the technique of Stainton et al. (1977). Filters were placed in glass vials and ashed in a muffle furnace at 550 °C for 1 hour to volatilize organic matter. Hydrochloric acid was then added to vials, which were then placed in a drying oven at 105 °C for 1 hour to convert the various P fractions to SRP, which was then assayed using the molybdenum blue technique. Suspended solids concentrations were quantified by passing water samples through pre-weighed Gelman AE filters, and then drying and re-weighing filters (+ 1 μg) using a Mettler UMT ultra-microbalance.

Precipitation data were obtained from a National Atmospheric Deposition Program (NADP) station located at Miami University's Ecology Research Center ~3 km north of Oxford, OH and ~5 km south of Acton Lake. We use the precipitation data mainly to establish general trends in annual precipitation so that we can evaluate how regional precipitation affects variation in nutrient flux among the three watersheds, rather than to construct nutrient budgets. Thus, although the precipitation station is located outside of our study watersheds, it is likely that the data are valid for our purposes.

Nutrient flux

One of our goals was to compare fluxes of dissolved, particulate and total nutrients among watersheds and years. Although we did not analyze all fractions in all years, we could estimate concentrations of unmeasured fractions because of strong relationships between certain fractions. For example, within a stream, concentrations of particulate C, N and P were highly correlated with the concentration of suspended solids (Table 3). Therefore, we estimated concentrations of particulate C and N (1997 and 1998) and particulate P (1998) using these regressions. Similarly, NO_3-N and TDN were highly correlated, as were SRP and TDP (Table 3). Therefore we estimated the concentrations of particulate nutrients, TDN, and TDP in this manner for samples when these fractions were not analyzed directly. We obtained total N (TN) concentrations by summing TDN and particulate N, and total P (TP) concentrations by summing TDP and particulate P.

Table 3. Parameters from linear regressions relating selected nutrient fractions and suspended solids in the three watersheds. All regressions were conducted on untransformed data. Units are μmol L^{-1} for all nutrient fractions and mg L^{-1} for suspended solids (SS)

		Marshall's Branch			Little Four Mile Creek			Four Mile Creek		
Independent Variable	Dependent Variable	Intercept	Slope	r^2	Intercept	Slope	r^2	Intercept	Slope	r^2
SRP	TDP	0.519	1.068	0.850	0.262	1.190	0.929	0.335	1.170	0.816
NO_3-N	TDN	38.767	1.040	0.786	36.319	1.013	0.946	63.267	1.004	0.821
SS	Particulate C	90.558	3.306	0.864	21.652	4.493	0.834	24.245	3.878	0.923
SS	Particulate N	10.222	0.222	0.827	9.375	0.270	0.893	8.273	0.187	0.924
SS	Particulate P	1.151	0.022	0.844	1.267	0.020	0.704	1.893	0.009	0.673

Hourly nutrient fluxes were calculated as the product of water discharge and nutrient concentration for that hour:

$$L_h = C_h \cdot Q_h$$

where L_h is hourly flux, Q_h is discharge, and C_h is concentration for hour h. If an hour contained a measured nutrient concentration, that measurement was assumed to apply to the entire hour. Concentrations for hours during which nutrient samples were not analyzed were interpolated from nearby sample points. Two interpolation methods were used: simple and Q-proportionate. Simple interpolation was used for NO_3-N:

$$C_h = C_{prev} + [(C_{next} - C_{prev}) \cdot ((h - h_{prev})/(h_{next} - h_{prev}))],$$

where C_{prev}, C_{next}, h_{prev} and h_{next} are the concentration and time of previous and next sample, respectively. For all other parameters interpolations were adjusted for variations in discharge, following the slope of the $log Q$-$log C$ regression, with residuals from that regression linearly interpolated through time and applied to the calculation of concentrations:

$$C_h = 10^{(R_h + B_0 + B_1 \log Q_h)}, \text{ and}$$

$$R_h = R_{prev} + [(R_{next} - R_{prev}) \cdot ((h - h_{prev})/(h_{next} - h_{prev}))],$$

where B_0 and B_1 are the intercept and slope of the $log Q$-$log C$ regression, and R_h is the interpolated residual from that regression. The method is essentially an automation of the standard technique that has been used for decades at sediment monitoring stations where samples are collected frequently (Porterfield 1972). It is appropriate here because of the high density of observed data points. There is no bias associated with retransformation of log-transformed data (Cohn 1995; Jansson 1985) because retransformations are not made from the regression line itself; rather, every point is adjusted with an appropriate residual prior to retransformation. Hourly nutrient fluxes were then summed to generate daily fluxes, which were summed across appropriate intervals to obtain monthly and annual fluxes. Flow-weighted mean concentrations were obtained as flux divided by discharge.

One of our goals was to assess interannual variation in nutrient flux, which is likely to be greatly affected by precipitation. Precipitation was much lower in 1994 than any other study year (see Results), so comparison of fluxes in 1994 to other years would likely yield very useful information. However, we did not begin sampling until 31 January 1994 (for SRP and NH_4-N) or 26 April 1994 (NO_3-N). Furthermore, the Little Four Mile Creek gaging station was not installed until 21 May 1994. To estimate discharge at Little Four Mile Creek before 21 May 1994, we used a regression using discharge from the Four Mile Creek station as the predictor variable. To estimate daily nutrient fluxes for the periods preceding our first sampling, we used stream-specific regressions of daily discharge vs. daily flux, using only dates on which concentrations were directly measured (i.e. we did not use interpolated daily fluxes to generate the regressions). For NO_3-N fluxes we used a linear regression with discharge, while for SRP and NH_4-N fluxes we used log-log regressions. We also wished to estimate flux of total N and P in 1994 (again, because precipitation was lowest in this year); however, we did not begin quantifying total dissolved nutrients, particulate nutrients or suspended solids until 1995. Thus we also estimated 1994 fluxes of particulate C, N and P as well as TDN and TDP with log-log regressions of daily discharge vs. daily flux (using 1995–1998 data). In all cases r^2 was > 0.65 and was usually > 0.8. We recognize that these regressions can sometimes yield biased estimates owing to retransformation biases, but we believe that it is instructive to compare fluxes in 1994 with those of other years.

Separation of nutrient flux via baseflow and stormflow

To help explain any differences in nutrient export among watersheds, we estimated the relative contributions of baseflow and stormflow to total discharge, and the proportions of nutrients exported in baseflow and stormflow. We conducted these analyses for nitrate-N, SRP and particulate P using January–June 1997 data. We used nitrate and SRP because we observed substantial differences among watersheds in the export coefficients of these nutrient fractions, and particulate P because the majority of P was exported in particulate form (see Results). We used 1997 data because in this year we directly quantified all three of these fractions and sampled streams daily for baseflow concentrations; this allowed relatively accurate determination of the timing of storm events. In addition, precipitation was more or less average for this year. We used data only through June because discharge was zero for a prolonged period between July and December.

To estimate the relative contributions of baseflow and stormflow to total stream discharge, we used the smoothed-minima technique of Gustard et al. (1992) as described in Jordan et al. (1997). First, daily discharge for the period (January–June 1997) was divided into non-overlapping 5-day blocks, and the minimum discharge obtained for each block. Then, each block minimum was compared with the minimum before and after. If 0.9 times the minimum was less than both of the neighboring minima, then that minimum was considered to be a measure of baseflow. Baseflow on intervening dates was obtained by linear interpolation. On dates in which estimated baseflow was greater than actual discharge, baseflow was redefined as the actual discharge on that day. A baseflow index was calculated as the sum of the daily baseflows divided by the total discharge for the entire period (January–June 1997). As others have pointed out (Jordan et al. 1997; Nathan & McMahon 1990), this and most other techniques used to estimate baseflow are somewhat arbitrary, and different techniques are likely to yield different absolute estimates of the baseflow index. However, different estimates are highly correlated and the use of a consistent technique allows comparison among watersheds, which is our primary objective.

To estimate nutrient flux via baseflow vs. flux via stormflow, we first obtained the concentrations before and after each storm event that could be characterized as reflective of baseflow conditions ('baseflow concentrations'). Baseflow concentrations were defined as those occurring when daily discharge was comprised of $\geq$ 80% baseflow. During storms, we linearly interpolated baseflow concentrations to obtain an estimated baseflow concentration for each date. Then, on each date we estimated nutrient flux via baseflow as baseflow discharge times baseflow concentration. Nutrient flux via stormflow was obtained as observed flux minus baseflow flux.

Statistical analyses

To statistically assess differences in nutrient concentrations and fluxes among watersheds, we conducted two types of analyses. To assess differences in concentrations, we used the Kolmogorov-Smirnov test (Sokal & Rolff 1981) to compare cumulative frequency distributions of monthly flow-weighted mean concentrations using each pairwise combination of streams (i.e. Four Mile vs. Little Four Mile, Four Mile vs. Marhsall's Branch and Little Four Mile vs. Marshall's Branch). We did these analyses for each nutrient fraction using data from all years. Because our study spanned 60 months, but streams were dry during a few months of this period, sample size was 55–60 for these analyses. Tests on flow-weighted mean concentrations are preferable to those on actual concentrations (i.e. using individual nutrient samples), because tests on actual concentrations are potentially subject to some bias if samples are missing from a given storm event for one or more streams (i.e. if an autosampler was temporarily not functioning) or because of unequal sample sizes among streams (e.g. at times Marshall's Branch was sampled more frequently because storm events occurred more rapidly).

We also used pairwise t-tests to quantify differences between pairs of streams in annual nutrient export coefficients (annual nutrient flux per unit watershed area); observations were paired according to years to control for inter-annual differences in flux driven by variation in precipitation.

Results

Precipitation, discharge and nutrient concentrations

Annual precipitation was lowest in 1994 (721 mm) and highest in 1996 (1227 mm; Table 4). On an annual scale, 1997 was also relatively dry (precipitation 845 mm), while 1995 (1009 mm) and 1998 (1031 mm) were close to the mean annual precipitation for this 5-yr period (967 mm) and to the region's long-term annual mean. Analysis of monthly data also shows that 1994 and 1996 were the most different in terms of precipitation. For example, precipitation was lower in 1994 than any other year during the calendar months of January, March, May, June and October (Table 4). There was no calendar month in which precipitation was maximal in 1994. In contrast, in the calendar months of April, May, September, November and December, precipitation was higher in 1996 than any other year, and there was no month in which precipitation was lowest. Mean discharge varied greatly among years, following trends in precipitation (Table 4). As expected in this climate, winter and spring were periods of highest discharge, and discharge was lowest in late summer and early fall.

Dynamics of discharge, NO_3-N, SRP and particulate P from four storm events and a two-week low-flow period in spring during 1997 are shown in Figure 2. These events are typical in terms of discharge and nutrient dynamics. SRP and particulate nutrient concentrations increased rapidly during storm-mediated discharge increases, and also rapidly recovered to pre-storm concentrations following storms (Figure 2). Daily variations in SRP and particulate P concentrations were minimal during low flow periods (Figure 2; note scale differences among time periods). At the beginning of a spring storm event, nitrate concentration usually showed a short-lived ($\sim$1 day) decrease as the hydrograph was rising. After this initial decrease, nitrate concentrations usually increased to pre-storm levels. During storms following extended low-flow periods, nitrate concentrations sometimes increased well above pre-storm concentrations after the initial decline in concentration. A May 1997 storm, which succeeded an unusually dry April, provides an example of these dynamics (Figure 2; Table 4). As discharge declined after storms, nitrate concentrations also declined, but much more slowly than dissolved or particulate P concentrations (Figure 2). Concentrations of certain fractions also varied greatly among streams. Concentrations of SRP were almost always higher in Marshall's Branch than the other two streams, during storms and low-flow periods. In contrast, NO_3-N concentrations were usually lowest in Marshall's Branch and highest in Little Four Mile Creek during all flow regimes (Figure 2). Differences among watersheds in particulate P

Table 4. Monthly precipitation data from the Miami University Ecology Research Center meteorological station, and mean discharge for the three study watersheds. Annual means and medians are for the 5-year period

	Precipitation (mm)						
Month	1994	1995	1996	1997	1998	Mean	Median
January	50.8	51.6	68.3	70.1	67.8	61.7	68.3
February	30.7	26.4	36.6	43.9	39.1	35.4	36.6
March	28.7	48.0	110.2	112.3	75.2	74.9	75.2
April	180.8	90.4	201.4	49.3	174.5	139.3	174.5
May	32.3	198.9	224.0	152.7	164.6	154.5	164.6
June	60.7	135.6	69.1	110.0	164.3	107.9	110.0
July	77.5	66.0	124.7	68.8	141.7	95.8	68.8
August	51.8	143.8	36.6	66.3	19.3	63.6	51.8
September	33.5	37.3	123.7	9.4	8.1	42.4	33.5
October	29.0	94.0	44.4	32.0	66.0	53.1	44.4
November	84.6	65.5	87.9	75.2	45.0	71.6	75.2
December	61.0	51.1	100.3	54.9	65.5	66.5	61.0
Annual	721.3	1008.7	1227.4	844.8	1031.3	966.7	1008.7
	Mean Discharge (m^3/sec)						
Watershed	1994	1995	1996	1997	1998	Mean	Median
Four Mile Cr.	0.866	1.292	3.139	1.131	1.219	1.529	1.219
Little Four Mile Cr.	0.523	0.624	1.761	0.975	1.315	1.040	0.975
Marshall's Br.	0.048	0.153	0.267	0.134	0.151	0.151	0.151

concentrations were more idiosyncratic and appeared to be storm-specific (Figure 2).

Flow-weighted mean nutrient concentrations also showed much variation seasonally and among streams. Monthly flow-weighted mean concentrations of all fractions tended to show some seasonality, but this was most pronounced for NO_3-N (Figure 3). Because NO_3-N comprised a large fraction of TN, TN also showed the same seasonality. Monthly flow-weighted mean NO_3-N concentration was almost always lowest in Marshall's Branch and highest in Little Four Mile Creek; differences between these two streams were often two-fold and were greatest at times of highest concentration (winter-spring; Figure 3). In contrast, Marshall's Branch usually exhibited the highest monthly flow-weighted mean SRP concentration (Figure 3).

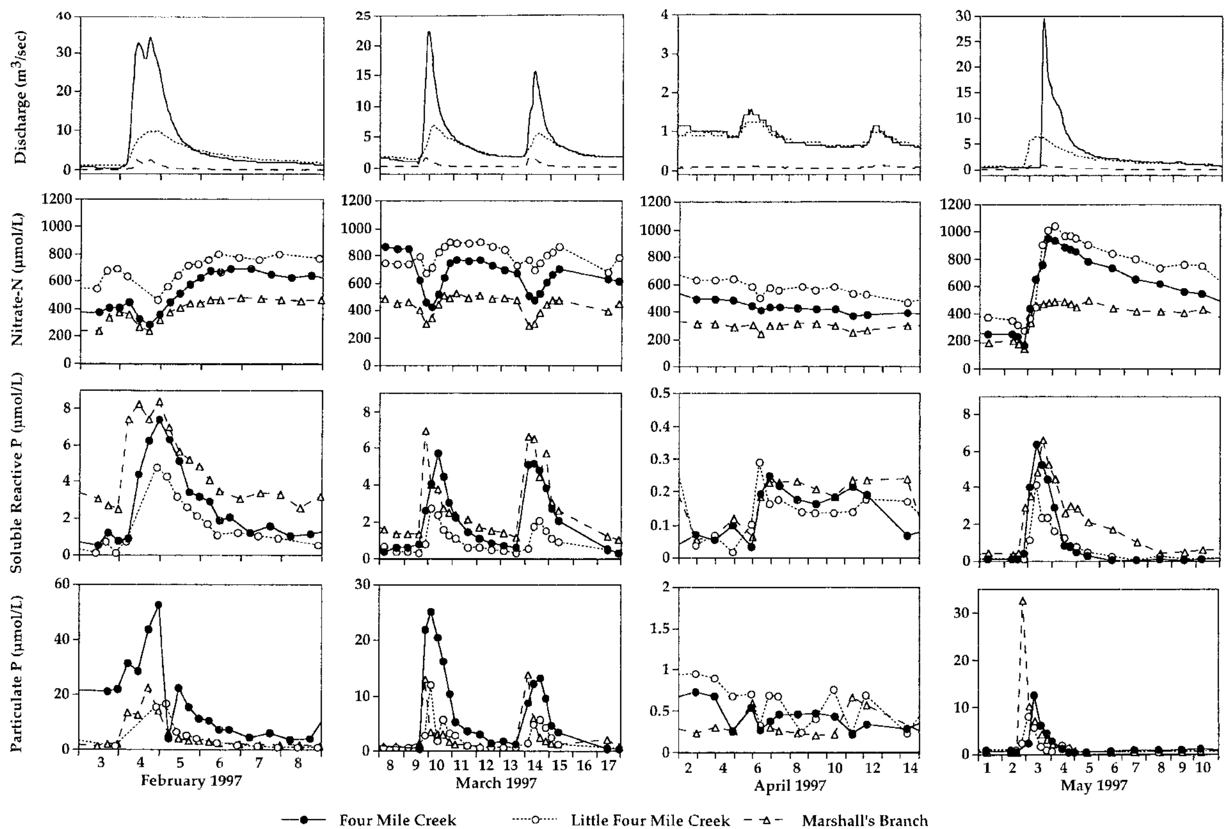

Figure 2. Discharge and concentrations of NO_3, soluble reactive P and particulate P in the three streams during four storm events and a spring low-flow period in 1997.

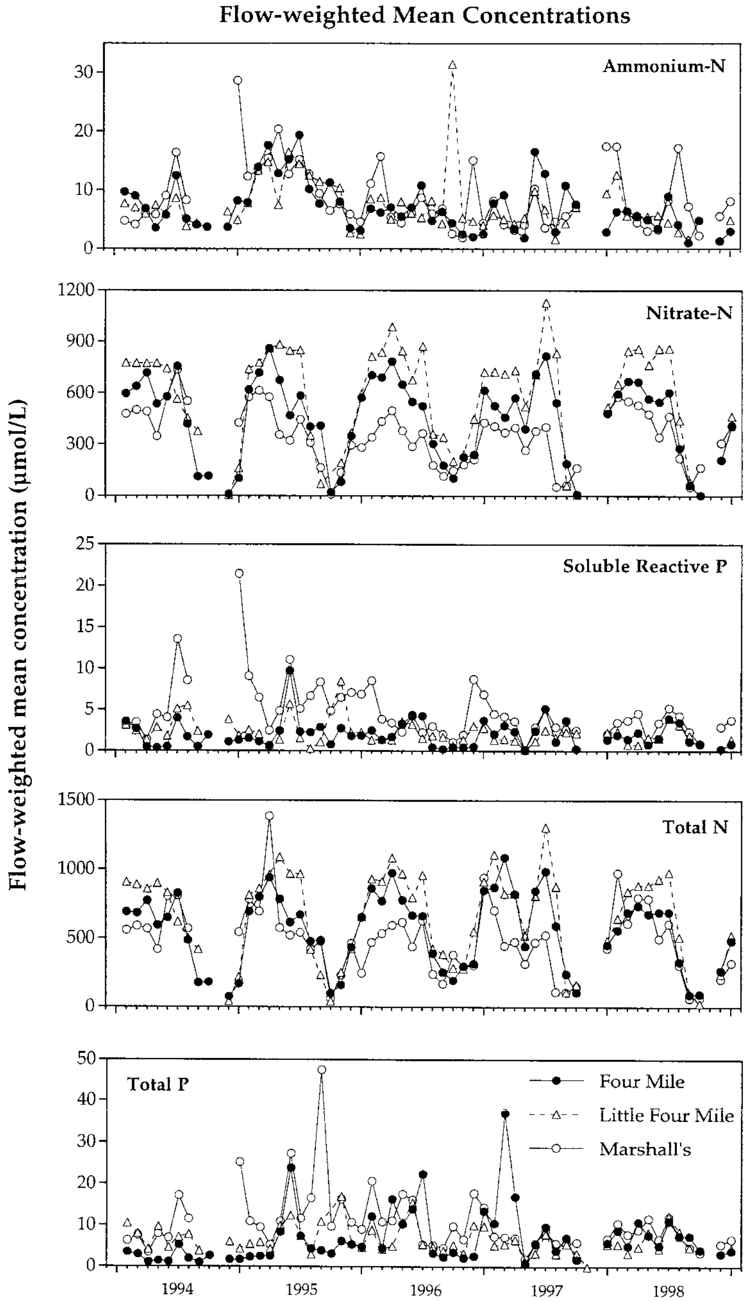

Figure 3. Flow-weighted mean concentrations for selected nutrient fractions for the three streams, 1994–1998. Breaks in lines represent time periods when streams were dry.

Results of the Kolmogorov-Smirnov tests revealed significant differences between watersheds in monthly flow weighted mean NO_3-N and SRP concentrations (Figure 4). Little Four Mile Creek had significantly higher monthly flow weighted mean concentrations of NO_3-N than Four Mile Creek ($P = 0.0446$) and Marshall's Branch ($P = 0.0081$). In addition, monthly flow weighted mean concentrations of NO_3-N were (marginally) significantly higher in Four Mile Creek than in Marshall's Branch ($P = 0.0552$). Patterns were similar for TDN except that Four Mile Creek and Marshall's Branch were not significantly different from each other (Figure 4). In contrast, Marshall's Branch had higher monthly flow weighted mean concentrations of SRP than Four Mile Creek ($P = 0.0081$) and Little Four Mile Creek ($P = 0.0124$), while concentrations in Four Mile Creek and Little Four Mile Creek were not significantly different from each other ($P = 0.2840$; Figure 4). Statistical differences were the same for TDP as for SRP (Figure 4). There were no statistically significant differences between streams in the monthly flow-weighted concentration of any other nutrient fraction (Figure 4).

Nutrient fluxes

Nutrient fluxes varied greatly over time and among watersheds (Figures 5–6). Monthly fluxes were generally higher in the first half of the year (January–June) than later in the year, for dissolved as well as total nutrient fractions (Figure 5). Within this general seasonal pattern, N and P fluxes appeared to show different temporal trends. Monthly nitrogen fluxes (NH_4-N, NO_3-N and total N) all tended to remain relatively high for several months early in each year, while P fluxes showed peaks of shorter duration in spring (Figure 5). Higher nutrient fluxes early in the year can be attributed to higher discharge, and for NO_3-N and total N, also to higher concentrations during this time.

Annual nutrient fluxes were also highly variable, and were correlated with precipitation and hence discharge. Thus, annual fluxes were generally highest in 1996, the wettest year, and lowest in 1994 or 1997, the two driest years (Figure 6; Table 4). Exceptions to this trend were the fluxes of particulate C and N in Four Mile Creek, which were high in 1997.

For all three watersheds, the majority of N was exported as NO_3-N (Figure 7). This percentage was highest in Little Four Mile Creek (87% of total N flux) and lowest in Marshall's Branch (70%). Relatively little N was exported as NH_4-N (< 2% in all watersheds). In Four Mile Creek and Marshall's Branch, particulate N accounted for $\sim$9% of total N flux, but in Little Four Mile Creek particulate N accounted for only $\sim$5% of N flux. Dissolved organic N (estimated as TDN – NO_3-N – NH_4-N) accounted for a greater percentage of N flux than NH_4 in all watersheds (and a greater percentage than particulate N in Little Four Mile Creek) but comprised < 20%

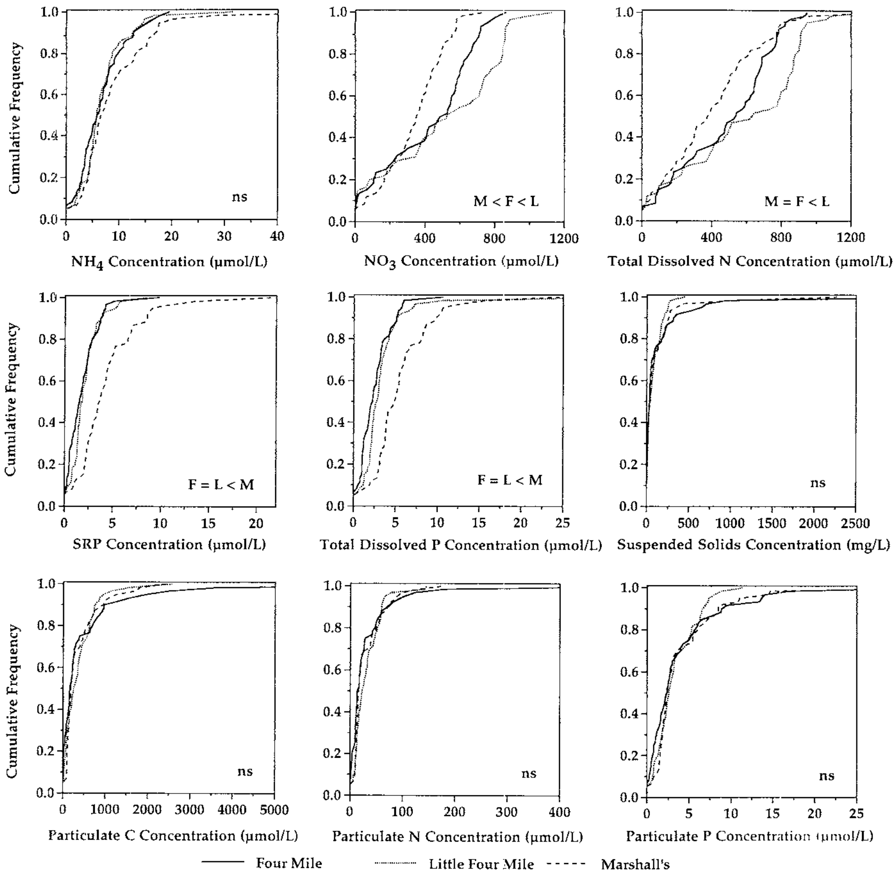

Figure 4. Plots of cumulative frequency of monthly flow-weighted mean nutrient and suspended solids concentrations over the entire 5-year period, and results of Komolgorov – Smirnov tests of the distributions. "ns" refers to no significant differences between streams ($P > 0.05$) in cumulative frequency distribution between pairs of streams. Letters indicate significant differences between streams (F = Four Mile Creek, L = Little Four Mile Creek and M = Marshall's Branch).

of N flux in all watersheds (Figure 7). For all three watersheds, most P was exported in particulate form (53–66% depending on watershed) and SRP comprised the second greatest fraction (27–37%; Figure 7). Soluble unreactive P (estimated as TDP – SRP) comprised a relatively small percentage of P flux (7–11%; Figure 7).

Nutrient flux per unit land area ('export coefficients') also varied among watersheds and years (Figure 8). SRP and TDP export coefficients were higher in Marshall's Branch than in Four Mile Creek ($P = 0.024$ for SRP; $P = 0.019$ for TDP; paired t-test) and Little Four Mile Creek ($P = 0.055$ for

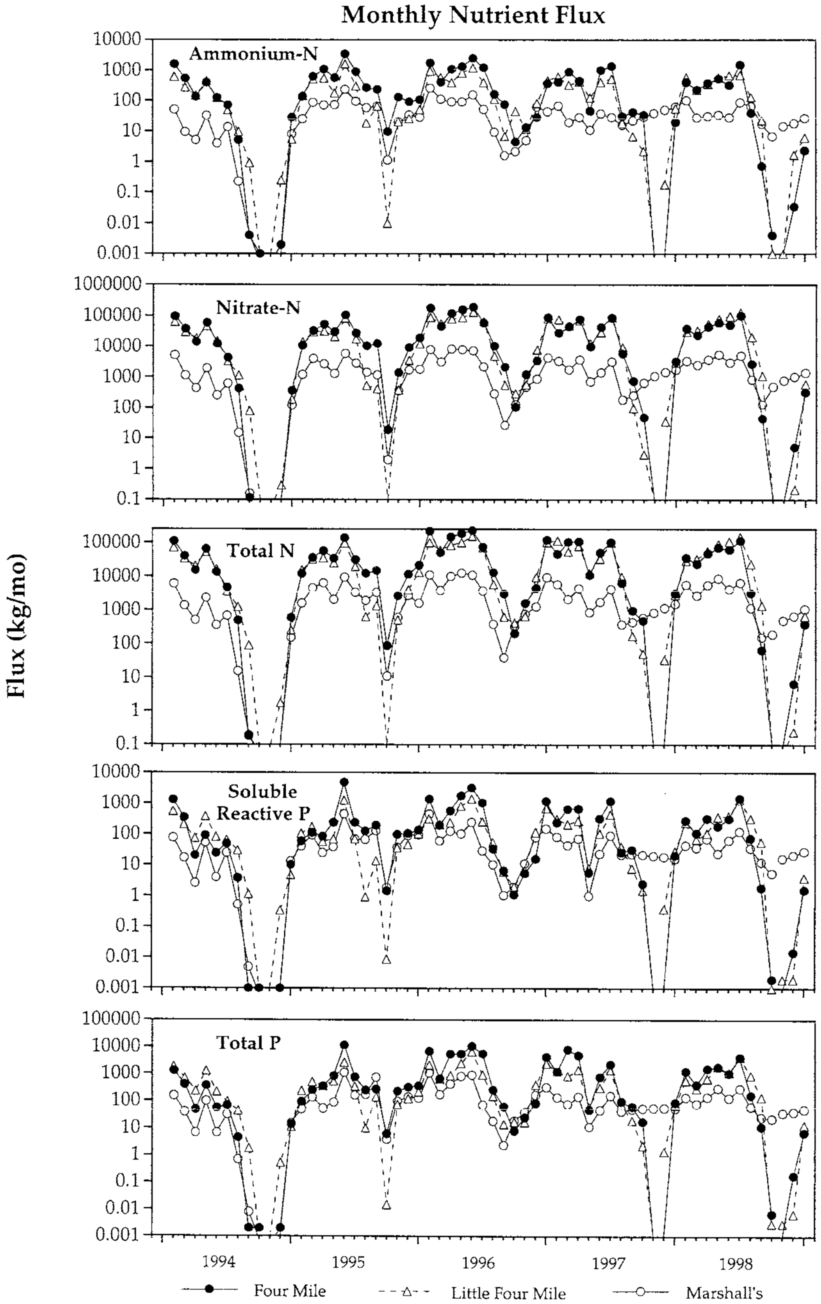

Figure 5. Monthly nutrient fluxes from the three watersheds, 1994–1998. Note log scale.

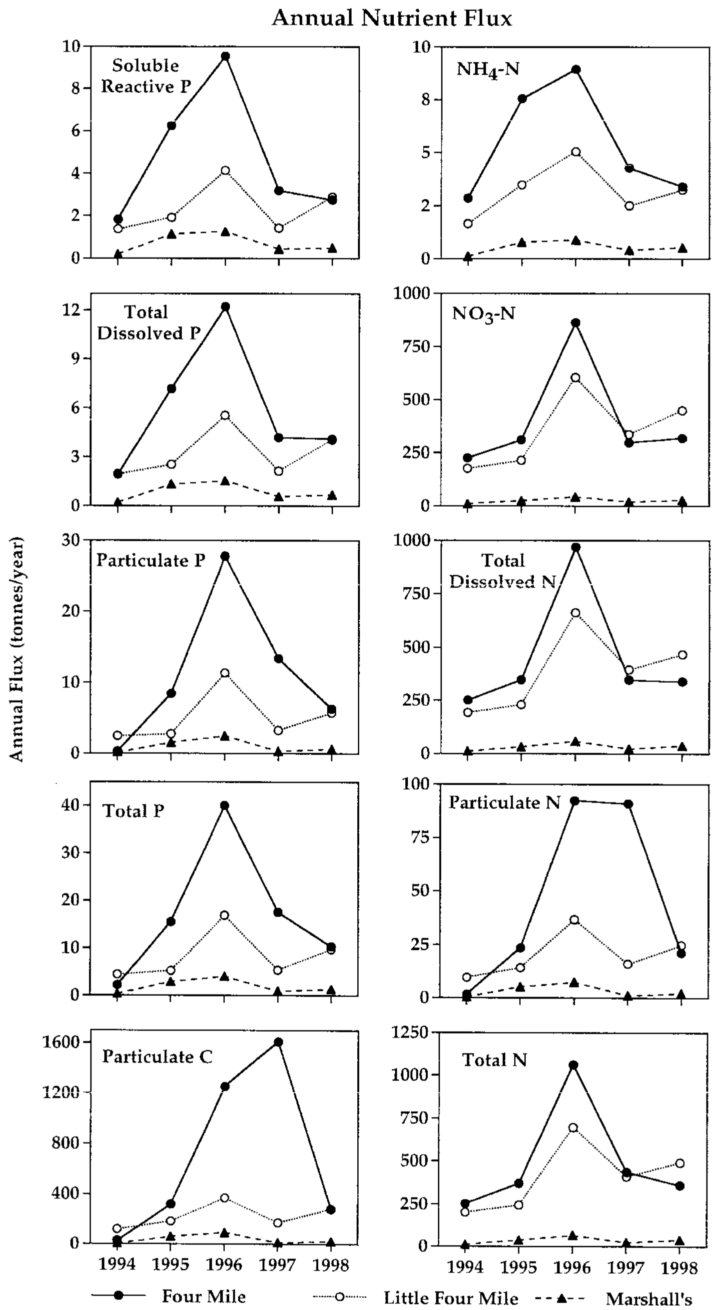

Figure 6. Annual nutrient fluxes from the three watersheds, 1994–1998.

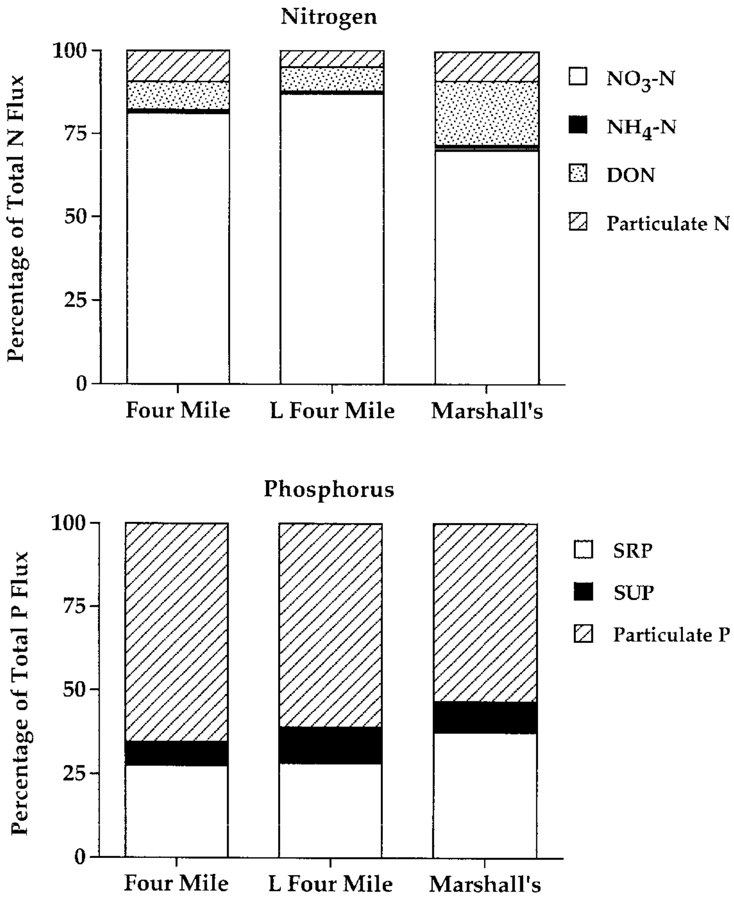

Figure 7. Percentage of total N and P fluxes comprised of various fractions. Data represent precentages over the entire 5-year period, 1994–1998.

SRP; P = 0.060 for TDP). Differences in export coefficients between Four Mile Creek and Little Four Mile Creek were not significant for SRP (P = 0.198) or TDP (P = 0.296). Averaged over the entire 5-year period, SRP and TDP export coefficients were 2.0 and 1.8 $\times$ higher, respectively, in Marshall's Branch than in Little Four Mile Creek. Relative among-watershed differences in SRP and TDP export coefficients seemed to be greater in wet years than in dry years (Figure 8). Differences among watersheds in TP export coefficients were not significant ($P > 0.13$ in all cases), partly because particulate P export coefficients were similar among watersheds ($P > 0.17$ in all cases; Figure 8).

Nitrogen export coefficients showed a pattern opposite that of dissolved P (Figure 8). NO_3-N and TDN export coefficients were significantly greater

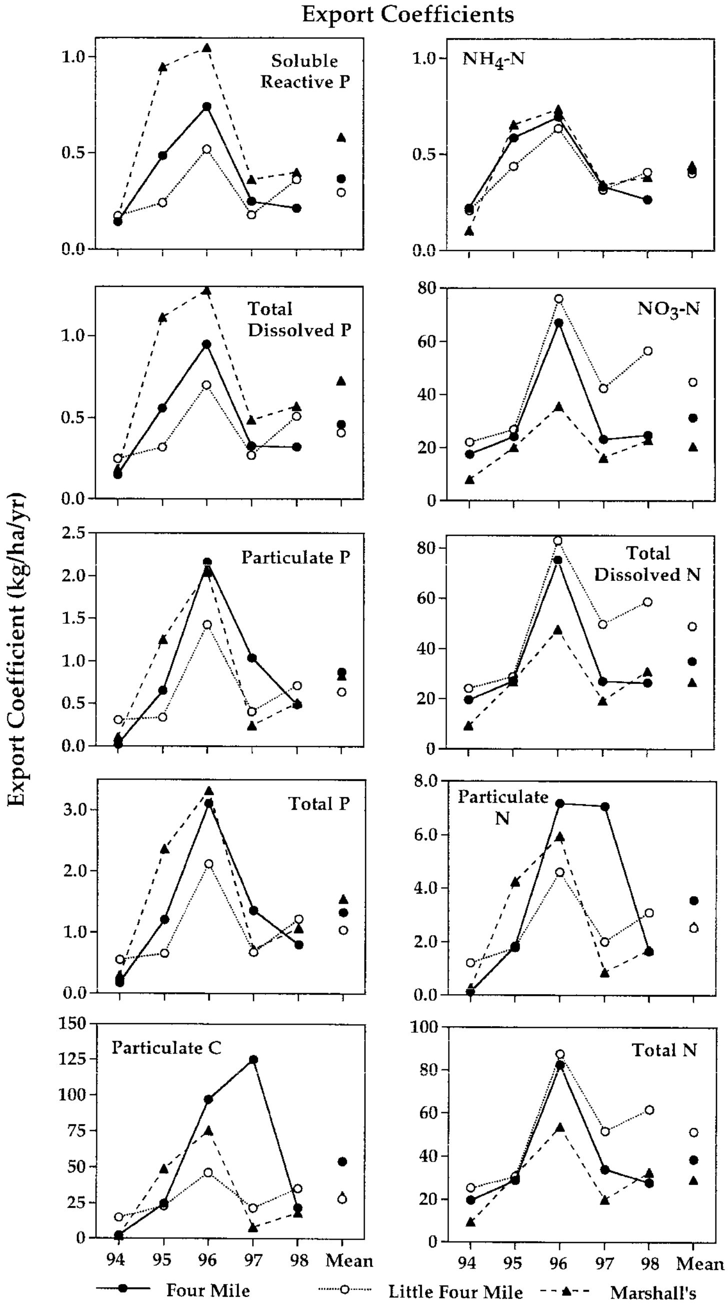

Figure 8. Annual nutrient flux per unit watershed area (export coefficients) for the three watersheds, 1994–1998. Mean represents the mean of the five annual export coefficients.

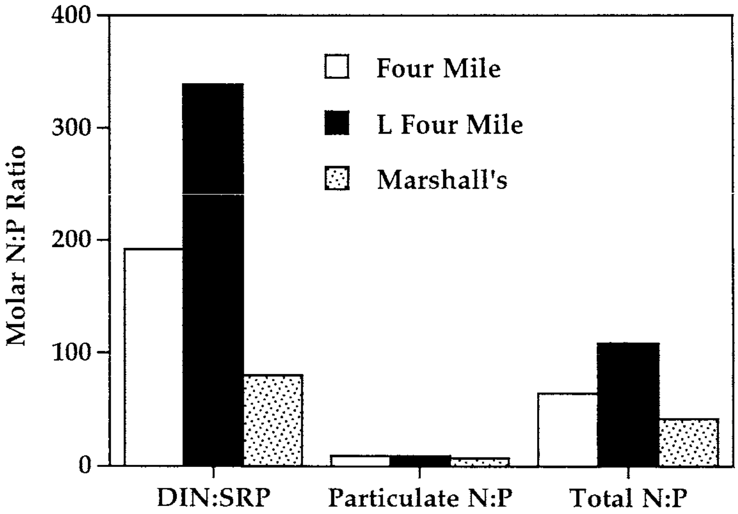

Figure 9. N:P ratio of fluxes of dissolved inorganic nutrients, total nutrients and particulate nutrients in the three watersheds. In each case the ratio is obtained as N flux divided by P flux over the entire 5-year period. DIN refers to dissolved in organic nitrogen.

in Little Four Mile Creek than in Four Mile Creek (P = 0.034 for NO_3-N and 0.039 for TDN) and Marshall's Branch (P = 0.009 for NO_3-N and 0.011 for TDN). Differences in export coefficients between Four Mile Creek and Marshall's Branch were either marginally significant (P = 0.056 for NO_3-N) or not significant (P = 0.104 for TDN). For TN, export coefficient was greater in Little Four Mile than in Four Mile (P = 0.047) and Marshall's Branch (P = 0.013), while those of Four Mile Creek and Marshall's Branch were not significantly different (P = 0.101). Averaged over the 5-year period, NO_3-N, TDN and TN export coefficients were 2.2, 1.8 and 1.7 $\times$ greater in Little Four Mile Creek than in Marshall's Branch, and differences among watersheds were evident in wet and dry years (Figure 8). No significant differences were found in the export coefficients of any particulate fraction (C, N, or P, or suspended solids; P > 0.10 in all cases).

The three watersheds showed substantial differences in the ratio at which N and P were exported (Figure 9). The ratio of dissolved inorganic N (NO_3-N + NH_4-N) to SRP exported from Little Four Mile Creek was > 4 $\times$ higher than in Marshall's Branch. Similarly, the TN:TP flux ratio was 2.6 $\times$ higher in Little Four Mile Creek than in Marshall's Branch (Figure 9). Particulate N:P export ratio was much lower, and varied little among watersheds (Figure 9).

Analysis of flow regimes from January–June 1997 showed that baseflow comprised a relatively greater proportion of total discharge in Little Four Mile Creek than in the other two streams. The baseflow index (sum of daily

Table 5. Baseflow index and the proportion of export as baseflow in the three study watersheds from January through June 1997. Baseflow index is defined as discharge via baseflow divided by total discharge

Watershed	Baseflow Index	Proportion of export in baseflow NO_3	SRP	Particulate P
Four Mile Creek	0.293	0.246	0.028	0.009
Little Four Mile Creek	0.437	0.376	0.132	0.081
Marshall's Branch	0.301	0.277	0.102	0.161

baseflows divided by the sum of daily total flows) was 0.437 for Little Four Mile Creek versus 0.293 in Four Mile Creek and 0.301 in Marshall's Branch (Table 5). In all streams, the majority of N and P were exported during storms. However, the proportion of N exported as baseflow was much greater than that for P. Thus, 24.6–37.6% of nitrate was exported as baseflow while only 2.8–13.2% of SRP and 0.9–16.1% of particulate P were exported as baseflow (Table 5).

Discussion

Our results are generally consistent with other studies of nutrient flux from agricultural watersheds. For example, other studies show that in watersheds dominated by agriculture, most P is exported in particulate form while most N is exported as nitrate (Logan 1990; Baker 1993). Export coefficients and flow-weighted mean concentrations for the Upper Four Mile Creek watersheds were generally within ranges reported from other agricultural watersheds (Baker 1993; Beaulac & Reckhow 1982; Cleresci et al. 1986; Cooke & Prepas 1998; Correll et al. 1999; Dillon & Kirchner 1975; Jordan et al. 1997a,b; Mueller et al. 1995; Puckett 1995). This is not surprising, as published export coefficients for a given nutrient fraction vary by more than one or two orders of magnitude. For example, considering only watersheds dominated by row crop agriculture, the studies cited above report export coefficients (kg ha^{-1} yr^{-1}) of 0.11–18.6 for TP, 0.04–2.2 for SRP, 2.1–80 for TN and 0.04–16.0 for NO_3-N. This is perhaps understandable, as many factors can vary among watersheds that are widely distributed geographically and studied under highly variable sampling programs. Our results show that nutrient fluxes varied considerably even among adjacent watersheds with essentially identical landuse patterns and climate. Furthermore, the extent to which fluxes differed among watersheds was dependent on the particular element or fraction under consideration. We emphasize that because we employed a very intensive, stratified sampling regime, which was identical among streams, our flux estimates are likely to be accurate and the variation we observe among watersheds is likely to be real.

Nitrate (and hence TN) export coefficients were highest in Little Four Mile Creek and lowest for Marshall's Branch. In contrast, SRP export coefficients were highest in Marshall's Branch and lowest in Little Four Mile Creek (Figure 8). One potential factor accounting for differences in NO_3 export is flow regime. Little Four Mile Creek had a greater baseflow index than the other two watersheds, and baseflow export was relatively more important for NO_3 than for P (Table 5). This concurs with Jordan et al. (1997), who found that NO_3 concentration increased with baseflow index for 27 Chesapeake Bay watersheds. They also found that baseflow index was not correlated with P concentrations. They attributed the differences in N and P to the fact that groundwater flow is more important for NO_3 flux than for dissolved P flux, consistent with our baseflow index data. Furthermore, Jordan et al. (1997) found that baseflow index had a greater effect on NO_3 concentrations in watersheds dominated by agricultural land than in watersheds with little or moderate amounts of agriculture. Thus, we would expect baseflow index to have relatively strong effects on NO_3 concentrations in our watersheds, all of which are > 90% agriculture. Thus it seems likely that Little Four Mile Creek had higher concentrations of NO_3 than the other two streams at least partly because of a greater contribution of groundwater flow. However, this cannot explain differences between Four Mile Creek and Marshall's Branch. These two streams had very similar baseflow indices but differed in NO_3 concentrations, although differences in NO_3 concentrations were not as great as the difference between Little Four Mile and the other two streams (Figures 4, 8).

Another possible factor contributing to higher NO_3 concentrations in Little Four Mile Creek is soil characteristics. The Little Four Mile Creek watershed contains soils that are overlain with thicker layers of loess (USDA 1992; Medley et al. 1995). Both Kahlkoff (1995) and Steinheimer et al. (1998) found that concentrations of TDN or NO_3-N in streams draining agricultural areas were positively correlated with the abundance of loess in the watersheds. Kahlkoff (1995) reasoned that the presence of a relatively thick loess layer above low-permeability geological units may result in increased lateral transport of TDN from groundwater to streams. Steinheimer et al. (1998) proposed that during surface runoff on the highly erodible loess layer, erosion associated with the raindrop impact continuously exposes nitrate to the overland flow path, eventually leading to high concentrations in streamflow. However, the Little Four Mile watershed also has soils that are less well-drained than the other two watersheds (USDA 1992). NO_3 concentrations are sometimes lower in watersheds with poorly drained soils compared to those with well-drained soils (Brenner & Mondrok 1995; Gambrell et al. 1975), perhaps due to greater nitrification rates in poorly drained soils (Groffman et al. 1992; Jordan et al. 1997).

One final potential factor contributing to higher NO_3 concentrations in Little Four Mile is a lower relative abundance of riparian forest. The Little Four Mile watershed has relatively less forest than the other watersheds (Table 1). Although differences among watersheds in the extent of forested area may seem minor, it is worth noting that nearly all of the forest in these watersheds is located in riparian areas. Even small riparian buffers can reduce NO_3 flux to streams, and forested buffers in agricultural watersheds seem more effective at reducing NO_3 flux than P flux (Osborne & Kovacic 1993).

The higher phosphorus export coefficient we observed for Marshall's Branch, the smallest watershed, agrees with other studies showing that P export coefficients are negatively correlated with watershed land area in agricultural catchments (Prairie & Kalff 1986; Soranno et al. 1996). However, we observed this trend only for dissolved P. Particulate and total P export coefficients varied greatly among years, but there was no apparent trend with watershed size (Figure 8). Furthermore, the size-related trend for dissolved P holds only when comparing Marshall's Branch with the other two watersheds; on average, dissolved P export coefficients were fairly similar in Four Mile and Little Four Mile (Figure 8). The negative correlations between P export coefficients and watershed area reported by others are not linear, and this may help explain the differences among the three UFMC watersheds with respect to P fluxes. Indeed, both Prairie and Kalff (1986) and Soranno et al. (1996) showed that TP export coefficients declined relatively sharply with watershed area for watersheds < 5000 ha , but that further increases in watershed size had little effect on P export coefficients. As both Four Mile and Little Four Mile Creek are substantially > 5000 ha, while Marshall's Branch is only $\sim$1200 ha, our results agree with these prior findings, but only for dissolved P.

Prairie and Kalff (1986) attributed the negative correlation between total P export coefficient and watershed size to increased drainage density (total length of streams per unit drainage area) as watershed size decreases, which was postulated to lead to increased export of particulate P from land to water (Prairie & Kalff 1986). However, size-related differences among our study watersheds were evident for dissolved P but not particulate P, and we observed no negative relationship between watershed area and particulate C and N export coefficients (Figure 8). In addition, SRP concentrations were higher in Marshall's Branch than other streams during low flow periods as well as during storms (Figure 2), suggesting that factors other than storm-related P delivery account for these area-related differences among watersheds.

Thus, differences in NO_3 export between watersheds may be at least partly attributable to differences in hydrologic regimes, soil characteristics and the extent of riparian forest. However, the reasons for higher SRP concentrations and export coefficients in Marshall's Branch are unclear. Whatever the mechanisms, the differences have potentially noteworthy implications. Differences of $\sim$2X in nutrient export coefficients may seem insignificant considering that in the literature these coefficients vary by over an order of magnitude in watersheds dominated by row crop agriculture, as mentioned above. However, a two-fold variation in nutrient export rate may have significant implications for water quality. A doubling of P loading rate to downstream lakes is predicted to increase lake TP by about 75%, with potentially concomitant increases in phytoplankton biomass (Smith 1998). In addition, Miltner and Rankin (1998) found that a doubling of stream DIN or TP concentrations can have substantial negative impacts on biotic integrity of small Ohio streams, as measured by either fish or invertebrate species composition. Finally, the variation we observed in N and P fluxes resulted in $\sim$4X variation among watersheds in the N:P ratio exported. This variation in N:P ratio may have important effects on the composition of algal assemblages in recipient ecosystems, especially in regards to cyanobacteria dominance (e.g. Downing et al. 1999; Hessen et al. 1997; Smith 1998). Thus, it seems that the differences we observed among watersheds are potentially important for the integrity of recipient ecosystems.

While strong and general trends between certain watershed characteristics and nutrient fluxes exist, it seems that these trends may be dependent on spatial scale. At regional scales, there are relatively strong relationships between watershed-scale factors and nutrient export. For example, N exports from large river systems can be successfully predicted using factors such as human population density, atmospheric N deposition, and land use (Caraco & Cole 1999; Howarth et al. 1996). At the other extreme, nutrient export from very small watersheds (e.g. plot-scale) can be successfully predicted using highly parameterized hydrological models (e.g. DeVantier & Feldman 1993; Grayson et al. 1992). However, often the scales relevant for ecosystem management are watersheds similar in size to those we investigate here (Naiman 1992; Naiman et al. 1995), and there is much variation among watersheds at these scales. More refined models, that account for factors such as spatial patterns of land use, the extent of riparian zones, and hydrological flow paths (e.g. Creed & Band 1998; Hunsaker & Levine 1995; Soranno et al. 1996), are needed to improve our ability to predict nutrient fluxes from watersheds of intermediate size.

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