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NUTRIENT DYNAMICS IN AN AGRICULTURAL WATERSHED: OBSERVATIONS ON THE ROLE OF A RIPARIAN FOREST[1]

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Abstract. Nutrient (C, N, and P) concentration changes were measured in surface runoff and shallow groundwater as they moved through a small agricultural (cropland) watershed located in Maryland. During the study period (March 1981 to March 1982), dramatic changes in water-borne nutrient loads occurred in the riparian forest of the watershed. From surface runoff waters that had transited ≈50 m of riparian forest, an estimated 4.1 Mg of particulates, 11 kg of particulate organic-N, 0.83 kg of ammonium-N, 2.7 kg of nitrate-N and 3.0 kg of total particulate-P per ha of riparian forest were removed during the study year. In addition, an estimated removal of 45 $kg \cdot ha^{-1} \cdot yr^{-1}$ of nitrate-N occurred in subsurface flow as it moved through the riparian zone.

Nutrient uptake rates for the cropland and riparian forest were estimated. These systems were then compared with respect to their pathways of nutrient flow and ability to retain nutrients. The cropland appeared to retain fewer nutrients than the riparian forest and is thought to incur the majority of its nutrient losses in harvested crop. The dominant pathway of total-N loss from the riparian forest seemed to be subsurface flux. Total phosphorus loss from the riparian forest appeared almost evenly divided between surface and subsurface losses.

Nutrient removals in the riparian forest are thought to be of ecological significance to receiving waters and indicate that coupling natural systems and managed habitats within a watershed may reduce diffuse-source pollution.

Key words: carbon; cropland; diffuse source pollution; groundwater; mass balance; nitrogen; nutrient cycling; phosphorus; riparian forest; surface runoff; watershed.

INTRODUCTION

Excessive nutrient loading can have significant ecological effects on the receiving waters of lakes (Edmondson 1972, Powers et al. 1972, Schelske and Stoermer 1972), streams (Hynes 1969), and estuaries (Fraser and Wilcox 1981, Myers and Iverson 1981). Nutrient loadings from managed watersheds have contributed an increasing amount of nutrients to receiving waters as agricultural practices have intensified and residential development has expanded to accommodate a growing human population. Furthermore, nutrient losses from agricultural lands represent both a monetary and energy loss to society.

In an effort to understand how nutrient loss is affected by internal watershed structure, Correll (1984) attempted to relate surface soil and subsoil composition to nutrient discharge for three watersheds of differing land use. Little or no correlation was found, and this was thought to indicate that significant nutrient transformations were occurring as water moved through the watersheds as surface runoff and groundwater. Thus, one objective of this study was to investigate nutrient (N, P, and C) transformations occurring as water moved through an agricultural (cropland and riparian forest) watershed as surface runoff and shallow groundwater. Another objective was to synthesize past data about this watershed to gain a better perspective of the overall nutrient dynamics of an agricultural ecosystem.

SITE DESCRIPTION

The study site is a small subwatershed of the 3,332-ha Rhode River drainage basin. The Rhode River lies within the mid-Atlantic Coastal Plain along the western shore of Chesapeake Bay ≈20 km south of Annapolis, Maryland (38°53′N, 76°33′W). The subwatershed studied (Fig. 1) is a 16.3-ha basin of which 10.4 ha was planted with corn. Cropland was tilled prior to planting and preemergent herbicides were used to control subsequent weed growth. Riparian forest and hedgerows were composed of broadleaved, deciduous trees and accounted for the remaining 5.9 ha. The soils are a fine sandy loam and are extremely deep (>600 m). An underlying clay layer (the Marlboro Clay) is thought to create an effective aquiclude near sea level for the entire basin (Chirlin and Schaffner 1977). At the weir the clay layer is at a depth of ≈2.0 m. Therefore, the site contains a perched, shallow aquifer. Soils above the aquiclude are noncalcareous and contain no phosphate minerals (Pierce 1982). Surface soil organic matter content and pH in the cultivated fields were 1.9% and 5.6, respectively, when measured in 1977. The basin slope is 5.44% and the channel slope is 2.65%.

MATERIAL AND METHODS

Sampling

Bulk precipitation for chemical analysis was continuously sampled at an elevation of 13 m at the central

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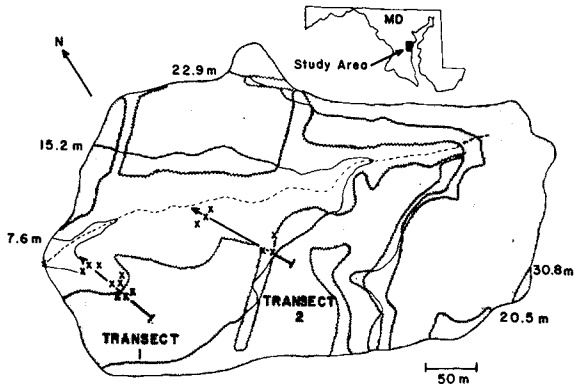

FIG. 1. General location of the study area (inset), and map of the watershed showing the positions of sampling transects (←) and goundwater wells (×). Shading indicates cultivated fields.

weather station for the Rhode River watershed (2.3 km from the study site). Collection was made in a clean polyethylene bottle fitted to a 28 cm diameter polyethylene funnel. Fiberglass window screen covered the funnel to keep insects out. Samples were collected following each rain event, and the sampler was cleaned and returned for use. The amount of rainfall was measured with a Belfort mass-recording rain gauge and a standard weather bureau manual gauge at the central weather station, and with a Steven's tipping-bucket gauge at the study site itself.

Stream discharge was monitored and water samples taken at a 120° sharp-crested V-notch weir, the foundation of which rested upon the Marlboro Clay layer. The associated instrument shed was equipped with a stilling well, depth monitor, and flow meter. The weir was built and instrumented in the spring of 1976 and both water and nutrient discharges have been measured since that time. Depth measurements were taken every 5 min and recorded as digital data on a punch tape. The flow meter was modified to close a sampling switch every 38 m^3 of discharge. Switch closure activated a sampling cycle in which a fixed volume of stream water was pumped from the base of the V-notch into sample containers. One sample bottle contained sulfuric acid preservative for biologically labile chemical species, the other contained no preservative. Samples were composited over weekly intervals for the 1-yr study period beginning in March 1981 and ending in March 1982. During a typical storm week over 2000 m^3 are discharged and over 50 samples taken. During a single, intense, summer storm that occurred during the study period 46 samples were taken in <12 h. During periods of very low discharge (<10 m^3/wk) weekly grab samples were taken. Quickflow and slowflow rates were calculated graphically from the hydrograph (Barnes 1940). In this paper we equate surface runoff with quickflow and subsurface or groundwater flows with slowflow. Subsurface (groundwater) flows in the system represent soil water percolation above the aquiclude. Seasons are defined in this paper as 3-mo periods (winter = December, January, and February).

Two transects of groundwater wells, ≈180 m apart, were established in the watershed (Fig. 1). Each transect consisted of several clusters of samplers at different elevations along the expected direction of flow. Each cluster consisted of a central groundwater well (piezometer) and two lateral wells located ≈10 m to either side and normal to the transect axis. Surface-water collectors located to collect only overland flow were associated with each groundwater well along transect 1. A total of 18 wells and nine surface water collectors were used. Surface-water collectors consisted of 4-L polyethylene bottles placed into holes in the soil in an inverted position. A rectangular slot was cut in the uphill side of the bottle at ground level and a short plastic apron was glued to the bottom of the slot and spread uphill to funnel surface flow into the bottle. Plastic tubing sealed into the cap of the inverted bottle allowed samples to be withdrawn without disturbing the sampler. Air was briefly bubbled through the sample to suspend particulates before the sample was withdrawn. Samplers were emptied prior to expected storm events and periodically cleaned. Groundwater wells consisted of 3.8 cm (inside diameter) polyvinyl chloride pipe perforated with 2.5-mm holes for ≈8 cm on the lower end. The bottom of the pipe was capped. Well holes were bored with a bucket auger either to the top of the Marlboro Clay or to a 4 m depth, whichever came first. Most wells were between 1.5 and 3.0 m deep. The pipes were inserted into the augered holes and clay packed around the pipe at the soil surface. The pipes extended ≈0.4 m above the ground and a loose cap was placed over the top. In all but one case the cluster of wells also had a fourth, shallower, groundwater well. On the day following a storm, water table heights were measured and wells pumped free of water. Samples were taken of the fresh groundwater the following day. When groundwater levels were low, equal volumes from each well within a cluster were composited to obtain enough sample for chemical analysis. Samples were returned to the laboratory and stored in the dark at 1.1°C. Aliquots for dissolved-nutrient determinations were filtered through prewashed Millipore HA membrane filters (0.45 μm nominal pore size) the day of collection and then returned to cold storage.

Nutrient analysis

Unfiltered rainfall samples were analyzed for nitrate, total Kjeldahl-N, ammonium-N, total-P, orthophosphate-P and organic matter concentrations. Surface runoff and groundwater samples were filtered and the filtrate analyzed for "dissolved" nitrite, nitrate, total Kjeldahl-N, ammonium-N, total-P, orthophosphate-P and organic matter concentrations. Unfiltered (whole) surface runoff samples were also analyzed for exchangeable ammonium-N, total Kjeldahl-N, ex-

changeable orthophosphate-P, total-P, total suspended particulate, and organic matter concentrations. Unfiltered, acidified, stream samples were analyzed for total Kjeldahl-N, ammonium-N, nitrate, total-P, orthophosphate-P, and organic matter.

Dissolved nitrite and nitrate were determined in nonacidified samples with a Dionex model 16 ion chromatograph. Nitrite and nitrate were determined in acidified samples by reduction on cadmium amalgam and colorimetry (APHA 1976). Since nitrite was present only in trace amounts, nitrite and nitrate are routinely summed and referred to as nitrate. Dissolved ammonium-N was determined by the oxidation of ammonia and labile amino compounds to nitrite and the subsequent colorimetric determination of nitrite (Richards and Kletsch 1964). Total Kjeldahl nitrogen, which includes ammonium nitrogen and organic amines, was determined by digestion with sulfuric acid and hydrogen peroxide (Martin 1972), distillation, and Nesslerization (APHA 1976). Organic nitrogen was calculated as the difference between total Kjeldahl nitrogen and ammonium nitrogen.

Dissolved total phosphorus was determined by a perchloric acid digestion (King 1932) and reaction with ammonium molybdate and stannous chloride (APHA 1976). Total phosphorus in unfiltered samples was determined by perchloric acid digestion, the development of a phosphomolybdic acid-blue complex and extraction of the blue complex with isobutyl alcohol (Correll and Miklas 1976). Determination of dissolved orthophosphate followed the same procedure used for dissolved total phosphorus except that samples were not digested.

Organic matter was measured as chemical oxygen demand (in milligrams per litre) (Maciolek 1962). An empirical conversion factor of 0.417 was used to obtain organic carbon concentration, in milligrams per litre. To determine extractable ammonium-N and orthophosphate-P, measured volumes of whole samples were filtered through polycarbonate nucleopore filters (0.4-μm pore size) and the particulate residue was washed with 1 mol/L KCl for ammonium-N or 0.5 mol/L HCl for orthophosphate-P. Following extraction and neutralization the same procedures used for the determination of dissolved ammonia and orthophosphate were followed. Suspended particulate concentration was calculated from the gain in mass of a prewashed, dried, and weighed millipore filter after filtration of a measured volume of sample. Filters both before and after filtration were dried for at least a week in a desiccator. All particulate parameters were calculated as the difference between concentrations found in unfiltered and filtered aliquots.

Vegetative sampling

In early April, 1982, prior to leafing out, $\approx$0.4 ha of the riparian forest near transect 1 was intensively sampled. The point-centered quarter technique (Cottam and Curtis 1956) was used to determine the relative dominance, density, frequency, size distribution, and importance value of the tree species present. Two increment cores were also taken from 130 of the 134 trees sampled. The average ring width was recorded for each tree and the dbh of the previous year calculated. The mean dbh for each of 13 size classes was then determined for the beginning and end of the study year. Weighted averages were calculated for both time periods using the number of trees in each size class as the weighting factor. These values and the allometric relations developed by Harris et al. (1973) were used to develop a rough estimate of the standing biomass of various tree components (branches, boles, large roots, and leaves). The difference in branch, bole, and root biomass prior and subsequent to the study year was considered the production of each component. Leaf production was considered to be the leaf biomass calculated by using the dbh at the end of the study period. Estimates of component biomass production were multiplied by the total density of trees and expressed in units of kilograms per hectare per year.

Cropland management, production, and nutrient uptake

Estimates of fertilizer applications and crop yields were obtained by direct inquiry from the farmer. These estimates were used in conjunction with data available from an intensive study in 1976–1978 that directly measured management inputs, crop nutrient uptake, crop production, and agricultural exports. A comparison of data obtained from the farmer with actual measurements of application rates showed an average difference of $\approx$2% for nitrogen and phosphorus.

Results

Mass balance

During the study period 10 040 m^3/ha of rainfall were measured. Of this 2540, 2970, 1890, and 2650 m^3/ha fell in the spring, summer, fall, and winter seasons, respectively (Table 1). The long-term (160-yr) average for seasonal precipitation in the Rhode River watershed is 2800, 3140, 2450, and 2460 m^3/ha in the spring, summer, fall, and winter, respectively (Higman and Correll 1982). Thus, seasonal precipitation was slightly above average in the winter, but below average for all other seasons. The net result was that annual rainfall was 800 m^3/ha below the long-term annual average.

Of the 10 040 m^3/ha of water that fell on the watershed during the study year, 23% was discharged in stream flow. Seasonally, 27, 13, 3.5, and 44% of precipitation inputs were discharged during the spring, summer, fall, and winter, respectively. Quickflow comprised 7.1% of the annual discharge and was greatest during the summer. Annual slow flow and quick flow measured during the study period were both below

TABLE 1. Watershed mass balances for the whole watershed in 1981–1982.

Season	Precipitation (100 m³/ha)*	Nutrient flux for watershed: Nitrate-N (kg/ha)	Ammonium-N (kg/ha)	Organic-N (kg/ha)	Total-P (kg/ha)	Orthophosphate-P (kg/ha)	Organic-C (kg/ha)
Bulk precipitation							
Spring	25.4	1.20	1.12	3.39	0.284	0.0584	13.9
Summer	29.7	1.26	0.785	1.43	0.0675	0.0252	11.2
Fall	18.9	0.95	0.540	0.111	0.0549	0.0349	5.67
Winter	26.5	1.36	0.385	1.67	0.0290	0.0190	5.58
Year	100.4	4.77	2.83	6.60	0.435	0.138	36.4
Long-term annual mean†	108.0 ± 21.8	4.79 ± 1.18	2.59 ± 0.56	6.01 ± 1.15	0.810 ± 0.278	···‡	43.1 ± 6.81
Management inputs							
Year	···	10.1	14.9	42.2	12.5	12.5	···
Watershed discharge	Slow flow / Quick flow (100 m³/ha)*						
Spring	6.26 / 0.687	0.532	0.197	0.577	0.251	0.116	153
Summer	3.20 / 0.804	0.428	0.0890	1.04	0.926	0.111	9.26
Fall	0.620 / 0.037	0.00675	0.00662	0.0264	0.0102	0.00656	0.424
Winter	11.5 / 0.119	1.53	0.0605	0.387	0.104	0.0548	3.56
Year	21.6 / 1.64	2.50	0.353	2.03	1.29	0.288	166
Long-term annual mean†	29.6 ± 13.9 / 4.97 ± 4.51	4.15 ± 3.06	0.434 ± 0.124	9.17 ± 10.2	1.72 ± 1.47	0.622 ± 0.407	58.2 ± 61.3

* Precipitation and stream flow expressed as 100 m³/ha is equivalent to the more traditional units of cm.

† 1973–1980 yearly means ± 1 SD for nitrogen bulk precipitation parameters (Correll and Ford 1982).
1973–1978 yearly means ± 1 SD for phosphorus and organic-C bulk precipitation parameters (D. L. Correll, *personal communication*).
1977–1981 yearly means ± 1 SD for nutrient and water discharge (D. L. Correll, *personal communication*).
Long-term (160-yr) yearly precipitation mean ± 1 SD for the vicinity of the Rhode River watershed (Higman and Correll 1982).

‡ ··· indicates no data are available.

their respective long-term means, but did fall within one standard deviation of their expected values (Table 1).

During the study year 14.2 kg/ha of total nitrogen (nitrate-N + ammonium-N + organic-N) was delivered to the watershed by bulk precipitation. Of this input of total nitrogen, 34% was nitrate-N, 20% ammonium-N, and 46% organic N. Input of total phosphorus by bulk precipitation was 0.435 kg/ha, of which 32% was orthophosphate-P. Organic-C dominated the measured inputs from bulk precipitation with an influx of 36.4 kg/ha. Nutrient inputs by bulk precipitation were all similar (±1 SD) to their respective long-term means, except for total phosphorus, which was almost half its expected value. When compared to the nutrient influx from bulk precipitation, management inputs were the most important source of nutrients to the system except for organic-C (Table 1). Management inputs occurred in three pulses of fertilizer application during the spring and summer of the study year.

The watershed as a whole discharged 17, 2, 4, and 10% of the total inputs of nitrate-N, ammonium-N, organic-N and total-P, respectively (Table 1). Output of organic-C was over four times the input in bulk precipitation. Seasonal area yield discharges ranged over an order of magnitude for all nutrients. Peak output occurred in the winter for nitrate-N; the spring for ammonium-N, orthophosphate-P, and organic-C; and the summer for organic-N and total-P.

Intrawatershed changes

Annual and seasonal average nutrient concentrations in surface runoff and groundwater are presented in Tables 2 and 3. In surface runoff flowing between the first and last clusters of samplers, reductions of 94, 78, 86, 84, 74 and 64% were observed in the mean annual total particulate, exchangeable ammonium-N, particulate organic-N, total particulate-P, exchangeable orthophosphate-P, and particulate organic carbon concentrations, respectively. Most of the total changes in concentration occurred within the first 19 m of riparian habitat. Dissolved nitrogen compounds in surface runoff also declined in concentration after traversing the riparian forest, with the greatest change occurring in the first 19 m. Total reductions of 79% for nitrate, 73% for ammonium-N, and 62% for organic-N were observed. The mean annual concentration of dissolved total phosphorus changed little in surface runoff. Dissolved organic carbon concentration increased 2.8-fold, but only 41% of this change occurred within the initial

TABLE 2. Seasonal and yearly mean nutrient concentrations in mg/L for surface runoff in watershed 109 (transect 1).

Position	Season	Total Sus. Part.	Nitrate-N	Ammonium-N Exch. Part.	Ammonium-N Diss.	Organic-N Part.	Organic-N Diss.	Total-P Part.	Total-P Diss.	Exch. Part. Ortho-phos-phate-P	Organic-C Part.	Organic-C Diss.
Entering riparian forest	Spring	8 840	3.73	0.734	3.63	27.7	1.47	3.22	0.256	0.354	67.2	12.1
	Summer	11 500	10.5	0.524	1.17	32.1	2.72	11.9	0.127	0.740	148.1	10.0
	Fall	3 830	1.57	0.301	0.896	16.8	0.779	3.29	0.128	0.863	101.1	6.75
	Winter*	1 760	1.99	0.048	0.250	1.32	2.04	0.860	0.320	0.675	63.2	19.1
	Year	6 480	4.45	0.402	1.49	19.5	1.75	4.82	0.208	0.658	94.9	12.0
19 m into riparian forest	Spring	1 380	2.60	0.218	1.23	6.47	1.18	2.31	0.081	0.456	35.9	12.0
	Summer	966	1.93	0.120	0.409	5.06	1.44	2.09	0.093	0.406	72.4	9.90
	Fall	122	0.343	0.038	0.069	2.61	0.529	0.604	0.393	0.134	5.97	4.09
	Winter*	176	2.18	0.042	0.158	0.37	1.33	0.065	0.375	0.108	···†	56.6
	Year	661	1.76	0.104	0.466	3.63	1.12	1.27	0.236	0.276	38.1	20.6
Leaving riparian forest	Spring	372	0.742	0.076	0.404	2.54	1.18	0.449	0.251	0.163	27.9	23.8
	Summer	524	1.03	0.108	0.175	3.46	0.713	1.04	0.183	0.244	45.6	16.0
	Fall	···	···	···	···	···	···	···	···	···	···	···
	Winter*	360	1.05	0.078	0.651	2.02	0.081	···	···	0.109	29.9	59.2
	Year	419	0.941	0.087	0.410	2.67	0.658	0.744	0.217	0.172	34.5	33.0

* Data from winter 1981. No samples were taken in winter 1982.
† ··· indicates no data are available.

portion of riparian forest. Although mean annual particulate concentrations of phosphorus, carbon, and organic-N in surface runoff decreased after moving through the riparian zone, the concentrations of these nutrients per unit of sediment increased. The effect of the riparian forest on particulate composition in surface runoff was to increase the proportion that was organic-C from 1.5 to 8.2%, organic-P (particulate total-P − exchangeable orthophosphate-P) from 0.064 to 0.14%, and organic-N from 0.30 to 0.64%. Furthermore, mean annual concentrations of exchangeable ammonium-N and orthophosphate-P per unit of sediment increased approximately two-fold after transit through the riparian zone. These results indicate that the particulates leaving the forest were more organic in composition and had a greater exchange capacity.

A t test was used to compare annual mean concentrations between the clusters of surface runoff collectors along transect 1. Noncomposited samples were used in the statistical analyses so that both spatial and temporal variability were included. Mean annual concentrations were significantly different ($P < .05$) between the first cluster (on the edge of the cropland) and the second cluster ($\approx$19 m into the riparian forest) for total suspended particulates, exchangeable ammonium-N, dissolved organic-N, total particulate-P, exchangeable orthophosphate-P, and particulate organic-C. Significant differences in mean annual concentrations between the second and third clusters were found for only nitrate-N and total particulate-P.

Another way of assessing the role of the riparian forest is to estimate the amount of nutrients or total particulates trapped or released per hectare. This was done by multiplying the change in mean concentration (concentration entering − concentration leaving) by the volume of surface runoff (quickflow) or groundwater flow (slow flow) measured at the weir for each season (see Tables 1–3). For surface runoff the result was that during the study year an estimated 4.13 Mg of particulates were trapped along with 0.219, 11.2, 2.98, 0.172 and 32.2 kg/ha of exchangeable ammonium-N, particulate organic-N, total particulate-P, exchangeable orthophosphate-P, and particulate organic-C, respectively. Calculated removals of dissolved nutrients in surface waters were 2.71, 0.827, and 0.568 kg/ha, respectively, for nitrate-N, ammonium-N, and organic-N, whereas 0.0160 kg/ha of dissolved total-P and 4.84 kg/ha of dissolved organic-C were released. These values are probably underestimates of the actual change in surface runoff loads because of reductions in surface flow due to evapotranspiration and/or infiltration in the riparian forest.

Surface runoff leaving the cropland had peak concentrations of total particulates, total particulate-P, and all nitrogen parameters in either the spring or summer. These concentration peaks thus corresponded with the time of fertilizer application and intense storm activity. Peak spring or summer concentrations were also apparent after runoff had traversed the 1st 19 m of riparian forest, but were less pronounced.

Changes in all mean annual groundwater concentrations while traversing the riparian zone were qualitatively similar for both transects, although differences in magnitude were evident (Table 3). In general, nitrate concentrations declined dramatically while ammonium-N increased in concentration. The remaining nutrient concentrations were relatively constant except for a four-fold increase in total-P along transect 1 and

TABLE 3. Seasonal and yearly mean nutrient concentrations in mg/L for groundwater in watershed 109.

Position	Season	Nitrate-N		Ammonium-N		Organic-N		Total-P		Organic-C	
		Transect 1	Transect 2	Transect 1	Transect 2	Transect 1	Transect 2	Transect 1	Transect 2	Transect 1	Transect 2
Entering riparian forest	Spring	5.43	5.78	0.097	0.058	0.312	0.226	0.024	0.120	1.41	1.36
	Summer	6.96	6.21	0.119	0.076	0.145	0.122	0.006	0.106	2.38	1.76
	Fall	6.89	7.22	0.045	0.132	0.169	0.121	0.016	0.152	1.97	1.90
	Winter	10.3	7.81	0.038	0.028	0.202	0.115	0.013	0.144	2.46	1.50
	Year	7.40	6.76	0.075	0.074	0.207	0.146	0.015	0.130	2.06	1.63
19 m into riparian forest	Spring	0.000	···*	0.098	···	0.213	···	0.012	···	2.43	···
	Summer	0.355	···	0.165	···	0.173	···	0.005	···	2.72	···
	Fall	0.282	···	0.114	···	0.214	···	0.018	···	1.82	···
	Winter	1.44	···	0.035	···	0.125	···	0.007	···	2.14	···
	Year	0.519	···	0.103	···	0.181	···	0.010	···	2.28	···
Leaving riparian forest	Spring	0.153	0.248	0.196	0.269	0.487	0.291	0.074	0.082	1.72	2.86
	Summer	0.453	0.000	0.498	0.478	0.223	0.419	0.065	0.378	2.81	4.58
	Fall	1.47	0.052	0.248	0.621	0.213	0.136	0.076	0.345	3.08	3.26
	Winter	0.978	0.105	0.156	0.396	0.144	0.125	0.032	0.183	2.77	3.08
	Year	0.764	0.101	0.274	0.441	0.267	0.243	0.062	0.247	2.60	3.44

* ··· indicates no data are available.

a two-fold increase in organic-C along transect 2. A 90% total decrease in the mean annual nitrate concentration was observed along transect 1 and a 98% decrease was observed along transect 2. Essentially all nitrate loss occurred within the first portion of riparian forest. Mean annual concentrations of ammonium-N increased in transect 1, with the overall increase being greater than three-fold. A six-fold increase occurred in transect 2. Overall, the annual average nitrate concentration declined 6.6 mg/L while traversing the forest, while the average concentration of combined forms of reduced nitrogen only increased by 0.36 mg/L. Thus, nitrate loss was apparently not due to its conversion into reduced forms of nitrogen that were measured.

Using a t test, comparisons were made to detect significant differences in mean annual groundwater concentrations between clusters of wells along each transect. Only noncomposited samples were used in the statistical analyses. Along transect 1 significant differences ($P < .05$) in mean annual concentrations between the first and second clusters were found only for nitrate-N, and between the second and third clusters for ammonium-N and total P. Significant differences between the two clusters along transect 2 were found for nitrate-N, ammonium-N, total-P, and organic-C.

The changes in concentration along transect 1, when related to seasonal groundwater discharge (slow flow; Table 1) give an estimated annual removal of 45.5 $kg \cdot ha^{-1} \cdot yr^{-1}$ of nitrate-N and an estimated release of 0.917, 0.194, 0.209, and 2.09 $kg \cdot ha^{-1} \cdot yr^{-1}$ of ammonium-N, organic-N, total-P, and organic-C, respectively, from the riparian forest. These values are probably underestimates because of reductions in subsurface flow due to evapotranspiration in the riparian forest.

Riparian vegetative production and nutrient uptake

Seventy-two percent of the sampled trees in the riparian forest were <22 cm in dbh, and the forest was clearly dominated by sweetgum (43.2% Importance Value) and red maple (16.0% I.V.) (Peterjohn 1982). Net primary production (NPP) was calculated as 18 600 $kg \cdot ha^{-1} \cdot yr^{-1}$ and was the sum of 5650 leaf, 3770 branch, 8100 bole, and 1030 large root production per hectare per year.

Estimates for the net production of respective tree components were multiplied by the mean midsummer (June, July, and August) nutrient concentrations found in a nearby forest (Table 4) and summed to estimate total nitrogen and phosphorus requirements. Sapwood concentrations were used for both branch and bole components. Uptake is defined as the annual elemental increment associated with the bole, branches, and large roots, plus the annual loss in leaf litterfall and throughfall. Nitrogen uptake by forest trees was calculated as ≈ 77 $kg \cdot ha^{-1} \cdot yr^{-1}$. Nitrogen return in leaf litter was calculated as 62 $kg \cdot ha^{-1} \cdot yr^{-1}$. Throughfall was not measured at the study site, so a literature value of 0.04 for the ratio of annual net nitrogen removal to foliage nitrogen content was used as an estimator (Henderson et al. 1977). Using this ratio, net nitrogen flux from leaves as throughfall was found to be 3.7 $kg \cdot ha^{-1} \cdot yr^{-1}$.

Using the same procedure employed for nitrogen, total phosphorus uptake by forest trees was calculated to be ≈ 9.9 $kg \cdot ha^{-1} \cdot yr^{-1}$. Phosphorus return in leaf litter was calculated as 7.8 $kg \cdot ha^{-1} \cdot yr^{-1}$. The flux of phosphorus from leaves as throughfall was estimated as 0.53 $kg \cdot ha^{-1} \cdot yr^{-1}$, using 0.06 as the ratio of annual net phosphorus removal to foliage phosphorus content

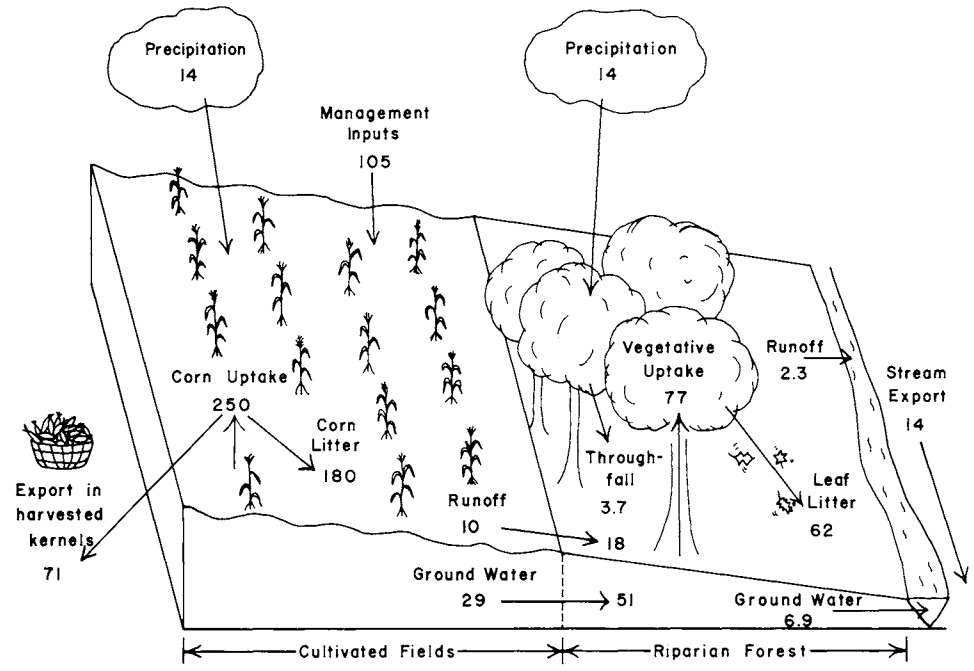

FIG. 2. Diagram of total-N flux and cycling in the study watershed from March 1981 to March 1982. All values are kilograms per hectare of the respective habitats (cropland and riparian forest/streams).

(Henderson et al. 1977). It should be emphasized that the uptake and production values presented are rough estimates. Nutrient uptake and turnover in the understory shrubs, herbaceous vegetation, and fine roots; nutrient return in branch, fruit, and flower litter; and whole-tree mortality were all factors not considered. Although rough, our production and uptake estimates are surprisingly reasonable when compared to literature values. Whittaker and Likens (1975) report 6000–25 000 kg·ha^{-1}·yr^{-1} as the normal range of NPP in temperate deciduous forests, and the mean uptake for 14 temperate deciduous International Biological Program sites has been reported as 75.4 kg·ha^{-1}·yr^{-1} of N and 5.6 kg·ha^{-1}·yr^{-1} of P by Cole and Rapp (1981). A measurement of 6350 kg·ha^{-1}·yr^{-1} for litter production in a nearby forest also compared well with our estimate of 5650 kg·ha^{-1}·yr^{-1} (D. F. Whigham, *personal communication*).

TABLE 4. Mean Kjeldahl-N and total-P concentrations (μg/g) in trees in a mature deciduous forest in the Rhode River watershed, Maryland.*

Tissue	Kjeldahl-N	Total-P
Midsummer (June, July and August)		
sapwood	814	99.9
large roots	1 567	441
leaves	16 300	1 551
Winter (November and January)		
sapwood	1 080	159
large roots	2 070	435
leaf litter (November only)	10 996	1 386

* Samples are from 1977. Species represented are *Liriodendron tulipifera, Fagus grandifolia, Acer rubrum, Liquidambar styraciflua, Nyssa sylvaticus,* and *Quercus falcata.*

Cropland management, production, and nutrient uptake

Limestone (1680 kg/ha) was applied to the agricultural fields in early April, granular 2-10-13 fertilizer in mid-April, liquid N and herbicides in mid-May and urea in mid-July. Of the 105 kg/ha of total-N applied; 63.0% was organic-N, 22.3% was ammonium-N, and 15.0% was nitrate-N. Total-P loading was 19.6 kg/ha. In 1976 and 1977, the respective loadings were 142 and 189 kg/ha of total-N, and 39.7 and 33.7 kg/ha of total-P. Thus, nutrient loadings for this study year were low when compared to previous years.

Crop nitrogen and phosphorus uptake, losses of nitrogen and phosphorus as annual harvest, and crop NPP were estimated using data from a previous study of the same watershed. The same farmer has cultivated this basin since 1970 and little change in farming practices has been observed. Nutrient uptake by corn plants (above and belowground) was measured directly in 1976 and 1977; N uptake was found to be ≈250 kg and P uptake 45.0 kg·ha^{-1}·yr^{-1} (Peterjohn 1982). The NPP of corn plants was also directly measured and found to be ≈24,000 kg·ha^{-1}·yr^{-1}. Nitrogen loss in harvested crop was estimated as 71.3 kg·ha^{-1}·yr^{-1} by multiplying the yield of 7.8 m^3 (222 bushels)/ha in 1981 by a 1976

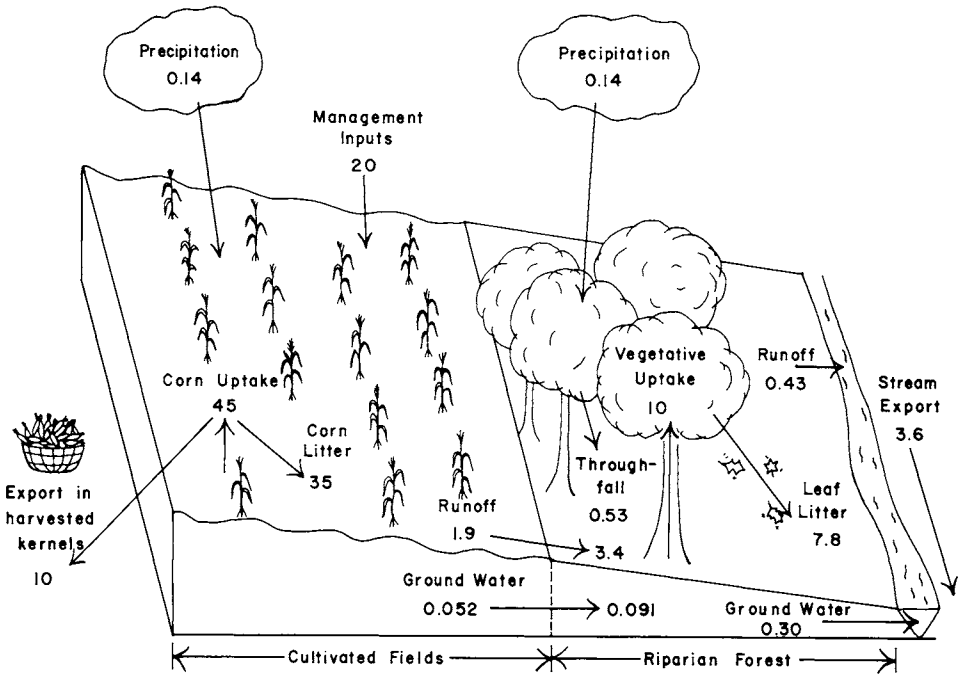

FIG. 3. Diagram of total-P flux and cycling in the study watershed from March 1981 to March 1982. All values are kilograms per hectare of the respective habitats (cropland and riparian forest/stream).

measurement of 33.3 kg of kernels per bushel, then multiplying the resultant product by a 1977 nitrogen measurement of 9.65 g/kg of kernels. Phosphorus loss in the harvested crop was estimated as 10.3 $kg \cdot ha^{-1} \cdot yr^{-1}$ using the same procedure. The value used for P content of kernels was 1.40 g/kg. Thus, only 28% of the total nitrogen and 22.9% of the total phosphorus uptake by corn plants was exported from the system in harvested kernels.

DISCUSSION

To synthesize information about the N and P dynamics of this watershed, two schematic diagrams were drawn (Figs. 2 and 3). Although the values presented are estimates with unknown error terms, these diagrams are useful to compare pathways of nutrient flux between and within habitats, and to develop falsifiable hypotheses for future research. It is important to note that flux estimates are given per unit area of each component habitat (cultivated fields or riparian forest). Thus, because there is 1.76× more cultivated land than riparian forest, N export from the agricultural habitat in groundwater was 29 kg/cultivated ha, whereas 51 kg/ha were gained by the riparian forest (Fig. 2).

The nitrogen dynamics for both the cultivated and riparian habitats are illustrated in Fig. 2. For the cultivated fields, input of total-N from bulk precipitation was small (12% of estimated total inputs) when compared to management applications. Of the estimated total nitrogen exports from the cropland, 64% (28% of corn uptake) was in harvested crop, 9.2% in surface runoff, and 26% in groundwater flow. Thus, the harvest seems to be the major pathway of total-nitrogen loss from the cropland. Groundwater appears to be the dominant pathway of total nitrogen flux between the cropland and riparian forest. Nitrogen retention (1 − outputs/inputs) for the cropland was calculated from our flux estimates and found to be low (8%), which is consistent with general ideas about disturbed ecosystems.

For the riparian forest, 17% of the estimated total-N inputs came in bulk precipitation, 61% in groundwater, and 22% in surface runoff. Of the estimated total-N losses from the riparian forest, 75% was lost in groundwater flow. Thus, it appears that the major pathway of nitrogen loss from the riparian forest was in subsurface flow. The calculated nitrogen retention by the riparian forest was 89%, and much higher than the retention of the cropland (8%).

The phosphorus dynamics for both the cultivated and riparian habitats are depicted in Fig. 3. For the cultivated fields, input of total-P from bulk precipitation was only 0.7% of the estimated total inputs. Of the estimated total phosphorus exports from the cropland, 84% (22% of corn uptake) was apparently lost in harvested crop, 16% in surface runoff and <1% in groundwater flow. Thus, the harvest seems to be the dominant pathway of phosphorus loss from the cropland, and surface runoff the dominant pathway of phosphorus flux between cropland and riparian forest. The

calculated phosphorus retention by the cropland was 41% and higher than the same value for total nitrogen.

For the riparian forest, 3.8% of the estimated total phosphorus inputs came in bulk precipitation, 94% in surface runoff, and 2.5% in groundwater flow. Unlike the loss of phosphorus from the cropland, phosphorus export from the riparian forest was nearly evenly divided between the estimated losses in surface runoff (59%) and groundwater flow (41%). The calculated phosphorus retention by the riparian forest was 80%. This value is twice as high as the retention by the cropland and slightly lower than the calculated total-nitrogen retention for the riparian zone.

From the observations made in this study two important questions arise: (1) What caused the decrease in groundwater nitrate concentration in the riparian forest? (2) How widely applicable are the effects we observed? Data from this study are insufficient to determine conclusively the reason for nitrate loss from groundwater in the riparian forest. Only two theoretical possibilities, however, appear likely: uptake by the vegetation and denitrification. To assess the approximate effect of vegetative uptake we estimated the annual incremental storage of N in the boles, branches, and large roots of the riparian trees. This was done by multiplying our production estimates by the mean winter tissue concentrations presented in Table 4. Winter tissue concentrations were used to correct for the effects of any retranslocation of nutrients from the leaves. From this calculation we estimate that N at the rate of 15 $kg \cdot ha^{-1} \cdot yr^{-1}$ was removed due to incremental growth, which, if true, accounts for only 33% of the nitrate-N removed from the groundwater. Considering that groundwater was sampled below the fine root zone at a depth of at least 1 m, it would seem that the occurrence of significant denitrification is a viable hypothesis.

An insufficient number of studies have been conducted to assess adequately how common the effects we observed are. Reductions in sediment loads and their associated nutrients in surface runoff should be a fairly universal effect of riparian forests because of the physical nature of the processes involved; a few studies present evidence that riparian zones reduce sediment and phosphorus loads in adjacent streams (McColl 1978, Schlosser and Karr 1981*a*, *b*). Nitrate removal from shallow groundwater is probably a biological process requiring an appropriate environment. Therefore, the extent to which riparian forests serve as sites of subsurface nutrient change is difficult to predict. It is encouraging to note, however, that results similar to those presented here (particularly subsurface nitrate-N removal) were obtained by a closely analogous study conducted in Georgia (Lowrance et al. 1984).

Nutrient loss from diffuse sources (such as cornfields) can have significant ecological effects which are generally understood as a threat to most bodies of water. Therefore, the estimated removal in surface runoff of 4.1 Mg of particulates, 11 kg of particulate organic-N, 0.83 kg of dissolved ammonium-N, 2.7 kg of nitrate-N and 3.0 kg of total particulate-P per hectare of riparian forest is potentially an extremely important ecological function. In addition, the removal of nitrate-N at an estimated rate of 45 kg/ha in subsurface flow is especially important. Release of this amount would have doubled the amount of nitrate-N discharged during the study year.

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LITERATURE CITED

APHA (American Public Health Association). 1976. Standard methods for the examination of water and waste water. 14th edition. American Public Health Association, New York, New York, USA.

Barnes, B. S. 1940. Discussion on analysis of runoff characteristics by O. H. Meyers. Transactions of the American Society of Civil Engineers **105**:104–106.

Chirlin, G. R., and R. W. Schaffner. 1977. Observations on the water balance for seven sub-basins of Rhode River, Maryland. Pages 277–306 *in* D. L. Correll, editor. Watershed research in eastern North America. Volume 1. Smithsonian Press, Washington, D.C., USA.

Cole, D. W., and M. Rapp. 1981. Elemental cycling in forest ecosystems. Pages 341–409 *in* D. E. Reichle, editor. Dynamic properties of forest ecosystems. Cambridge University Press, Cambridge, England.

Correll, D. L. 1984, *in press*. N and P in soils and runoff of three coastal plain land uses. *In* R. L. Todd, R. Leonard, and L. Assmussen, editors. Nutrient cycling in agroecosystems. University of Georgia Press, Athens, Georgia, USA.

Correll, D. L., and D. Ford. 1982. Comparison of precipitation and land runoff as sources of estuarine nitrogen. Estuarine, Coastal and Shelf Science **15**:45–56.

Correll, D. L., and J. J. Miklas. 1976. Phosphorus cycling in a Maryland deciduous forest subjected to various levels of mineral nutrient loading. Pages 642–657 *in* F. G. Howell, J. B. Gentry, and M. H. Smith, editors. Mineral cycling in southeastern ecosystems. Symposium Series (CONF-740513), Energy Research and Development Administration, Washington, D.C., USA.

Cottam, G., and J. T. Curtis. 1956. The use of distance measures in phytosociological sampling. Ecology **37**:451–460.

Edmondson, W. T. 1972. Nutrients and phytoplankton in Lake Washington. American Society of Limnology and Oceanography Special Symposium **1**:172–188.

Fraser, T. H., and W. H. Wilcox. 1981. Enrichment of a subtropical estuary with nitrogen, phosphorus and silica. Pages 481–498 *in* B. J. Neilson and L. E. Cronin, editors. Estuaries and nutrients. Humana, Clifton, New Jersey, USA.

Harris, W. F., R. A. Goldstein, and G. S. Henderson. 1973. Analysis of forest biomass pools, annual primary production and turnover of biomass for a mixed deciduous forest watershed. Pages 41–46 *in* H. Young, editor. Proceedings of the working party on forest biomass of IUFRO. University of Maine Press, Orono, Maine, USA.

Henderson, G. S., W. F. Harris, D. E. Todd, and T. Grizzard. 1977. Quantity and chemistry of throughfall as influenced by forest-type and season. Journal of Ecology **65**:365–374.

Higman, D., and D. L. Correll. 1982. Seasonal and yearly variation in meterological parameters at the Chesapeake Bay Center for Environmental Studies. Pages 1–159 *in* D. L. Correll, editor. Environmental data summary for the Rhode River ecosystem. Volume A, Part I. Chesapeake Bay Center for Environmental Studies, Edgewater, Maryland, USA.

Hynes, H. B. N. 1969. The enrichment of streams. Pages 188–196 *in* Eutrophication: causes, consequences, correctives. National Academy of Sciences, Washington, D.C., USA.

King, E. J. 1932. The colorimetric determination of phosphorus. Biochemical Journal **26**:292–297.

Lowrance, R. R., R. L. Todd, and L. E. Asmussen. 1984. Nutrient cycling in an agricultural watershed: I. Phreatic movement. Journal of Environmental Quality **13**:22–27.

Maciolek, J. A. 1962. Limnological organic analyses by quantitative dichromate oxidation. Fish and Wildlife Service Publication, Washington, D.C., USA.

Martin, D. F. 1972. Marine chemistry. Volume 1. Marcel Dekker, New York, New York, USA.

McColl, R. H. S. 1978. Chemical runoff from pastures: the influence of fertilizer and riparian zones. New Zealand Journal of Marine and Freshwater Research **12**:371–380.

Myers, V. B., and R. I. Iverson. 1981. Phosphorus and nitrogen limited phytoplankton productivity in northeastern Gulf of Mexico coastal estuaries. Pages 569–582 *in* B. J. Neilson and L. E. Cronin, editors. Estuaries and nutrients. Humana, Clifton, New Jersey, USA.

Peterjohn, W. T. 1982. Nutrient transformations in three single-land-use watersheds. Thesis. Miami University of Ohio, Oxford, Ohio, USA.

Pierce, J. W. 1982. Geology and soils of the Rhode River Watershed. Pages 181–216 *in* D. L. Correll, editor. Environmental data summary for the Rhode River ecosystem. Volume A, Part I. Chesapeake Bay Center for Environmental Studies, Edgewater, Maryland, USA.

Powers, C. F., D. W. Schults, K. W. Malueg, R. M. Brice, and M. D. Schuldt. 1972. Algal responses to nutrient additions in natural waters. American Society of Limnology and Oceanography Special Symposium **1**:141–154.

Richards, F. A., and R. A. Kletsch. 1964. The spectrophotometric determination of ammonia and labile amino compounds in fresh- and seawater by oxidation to nitrite. Pages 65–81 *in* Sugawara festival volume. Maruza, Tokyo, Japan.

Schelske, C. L., and E. F. Stoermer. 1972. Phosphorus, silica, and eutrophication in Lake Michigan. American Society of Limnology and Oceanography Special Symposium **1**:157–170.

Schlosser, I. J., and J. R. Karr. 1981*a*. Water quality in agricultural watersheds: impact of riparian vegetation during base flow. Water Resources Bulletin **17**:233–240.

Schlosser, I. J., and J. R. Karr. 1981*b*. Riparian vegetation and channel morphology impact on spatial patterns of water quality in agricultural watersheds. Environmental Management **5**:233–243.

Whittaker, R. H., and G. E. Likens. 1975. The biosphere and man. Page 306 *in* H. Lieth and R. H. Whittaker, editors. Primary productivity of the biosphere. Springer-Verlag, New York, New York, USA.