

Relating nutrient discharges from watersheds to land use and streamflow variability

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Abstract. During a 1-year period we measured discharges of water, suspended solids, and nutrients from 27 watersheds having differing proportions of cropland in the Piedmont and Coastal Plain provinces of the Chesapeake Bay drainage. Annual flow-weighted mean concentrations of nitrate and organic N and C in stream water correlated with the relative proportions of base flow and storm flow. As the proportion of base flow increased, the concentration of nitrate increased and the concentrations of organic N and C decreased. This suggests that discharge of nitrate is promoted by groundwater flow but discharges of organic N and C are promoted by surface runoff. Concentrations of N species also increased as the proportion of cropland increased. We developed a statistical model that predicts concentrations of N species from the proportions of cropland and base flow. P concentrations did not correlate with cropland or base flow but correlated with the concentration of suspended solids, which differed among watersheds.

1. Introduction

Over the past few decades, riverine discharges of plant nutrients have increased in response to enormous increases in anthropogenic inputs. For example, increases in discharges of nitrogen and phosphorus from the Mississippi basin have been linked to the respective twentyfold and fourfold increases in applications of nitrogen and phosphorus fertilizers since 1940 [Turner and Rabalais, 1991]. Discharge of nitrogen from rivers throughout the United States and Europe correlates with the sum of anthropogenic inputs from fertilizer application, cultivation of nitrogen-fixing crops, net imports of agricultural products, and fossil fuel combustion [Jordan and Weller, 1996; Howarth et al., 1996]. Because much of the anthropogenic nutrient input is related to agriculture, watersheds with greater proportions of agricultural land tend to discharge greater amounts of nitrogen [Hill, 1978; Neill, 1989; Mason et al., 1990], phosphorus [Dillon and Kirchner, 1975], or both nutrients [Rekolainen, 1990; Correll et al., 1992; Nearing et al., 1993; Kronvang et al., 1995]. Consequently, agricultural land use is an important factor in many empirical models of nutrient discharge [Osborne and Wiley, 1988; Hunsaker and Levine, 1995; Johnson et al., 1997].

Nutrient discharges are also influenced by mechanisms of water flow from the land. Rapid surface flows of water that enhance erosion are likely to enhance transport of phosphorus, which is mostly bound to particulate matter [Dillon and Kirchner, 1975; Grobler and Silberbauer, 1985]. In contrast, rapid infiltration and groundwater flows are likely to enhance transport of nitrate, which is very soluble and easily leached from the soil. Groundwater contamination with nitrate is more common beneath well-drained soils [e.g., Spalding and Exner, 1993], while consumption of nitrate by denitrification is greater in poorly drained soils [Gambrell et al., 1975]. Discharge of nitrate in streams has been related to a groundwater delivery

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factor that reflects the leaching potential of soils in the watersheds and the hydraulic conductivity of the aquifers [Brenner and Mondok, 1995].

Understanding the factors that influence nutrient discharge is critical to understanding the eutrophication of lakes, estuaries, and coastal waters, which has been accelerated throughout the world by anthropogenic nutrient inputs [Nixon, 1995]. In the Chesapeake Bay, one of the world's largest estuaries, anthropogenic increases in watershed inputs of both nitrogen and phosphorus have led to excessive plankton production [Malone et al., 1986, 1988; Boynton et al., 1982; Correll, 1987; Jordan et al., 1991a, b; Fisher et al., 1992; Gallegos et al., 1992] that has contributed to the demise of submerged aquatic vegetation [Kemp et al., 1983] and an increase in the extent of hypoxic waters [Taft et al., 1980; Officer et al., 1984]. Excessive nitrogen and phosphorus inputs also lead to seasonal depletion of dissolved silica and result in altered phytoplankton production and species composition in the mid to lower bay [D'Elia et al., 1983; Anderson, 1986; Conley and Malone, 1992]. The Chesapeake Bay watershed contributes approximately two thirds of the nitrogen, one quarter of the phosphorus, and all of the silica inputs to Chesapeake Bay [Correll, 1987]. Agriculture is the main source of nitrogen discharge from the watershed of Chesapeake Bay [e.g., Fisher and Oppenheimer, 1991; Jaworski et al., 1992].

The 178,000-km² watershed of Chesapeake Bay extends over three physiographic provinces, the Coastal Plain, the Piedmont, and the Appalachian, which differ in land use patterns, topography, hydrology, and geology. About 18% of the watershed, including all of the land adjacent to the shoreline, is in the Coastal Plain [National Center for Resource Innovation (NCRI), 1982], which is low-lying land consisting of layers of unconsolidated marine sediments with differing grain sizes and permeabilities. The Coastal Plain includes a variety of land uses. Along the eastern shore of the Chesapeake are areas where production of corn and soybeans matches that of the central U.S. corn belt [Thomas and Gilliam, 1977]. Farther south on the Delmarva Peninsula, one of the largest concentrations of poultry farms in the United States produces a very

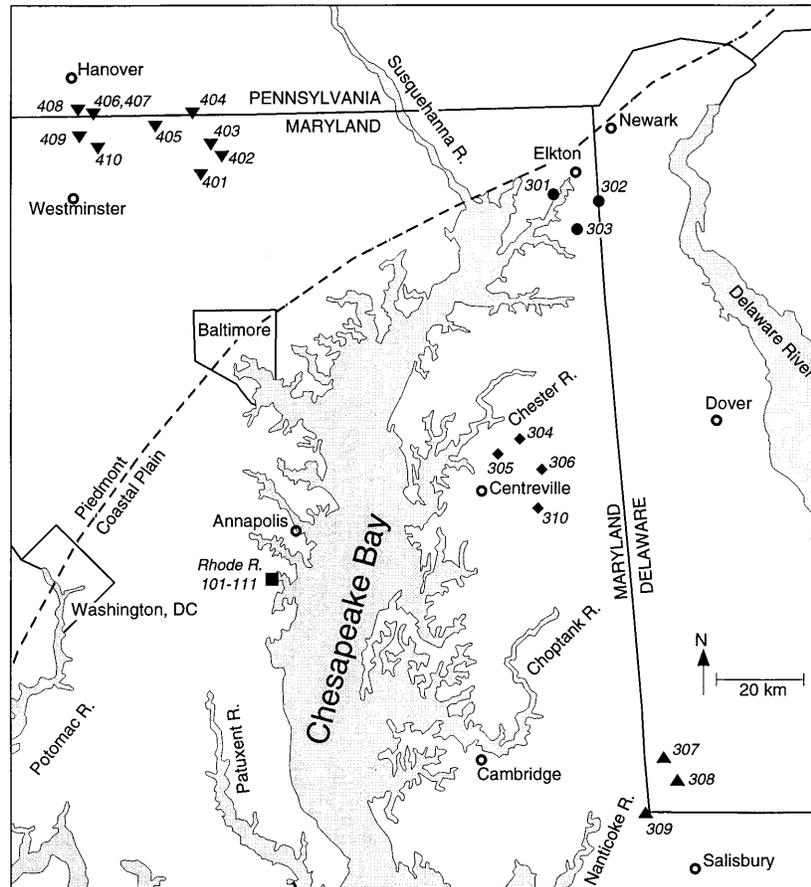


Figure 1. Locations of the 27 numbered study watersheds including 7 watersheds of the Rhode River on the inner Coastal Plain (square), 3 more inner Coastal Plain watersheds on the northern Delmarva Peninsula (solid circles), 4 central Coastal Plain watersheds (diamonds), 3 outer Coastal Plain watersheds (triangles), and 10 Piedmont watersheds (inverted triangles) north of Baltimore, Maryland.

serious problem of manure disposal [Sims and Wolf, 1994]. On the western shore of the Chesapeake, agriculture is a less predominant land use than on the eastern shore. The topography of the Coastal Plain varies from rolling hills on the inner Coastal Plain on the western shore and on the northern end of the Delmarva Peninsula, to the extremely flat terrain of the outer Coastal Plain on the southern end of the Delmarva Peninsula.

Twenty-five percent of the Chesapeake watershed is in the Piedmont [NCRI, 1982], a hilly, uplifted peneplain underlain mainly by metamorphic rocks including quartzites, gneisses, schists, and marbles [Hunt, 1974; Thornbury, 1965]. The Piedmont is a potentially important source of nutrients to the Chesapeake Bay because it includes about 25% of the cropland in the Chesapeake watershed [NCRI, 1982]. The main crops are corn, soybeans, alfalfa, and wheat; livestock production is mainly dairy [Bureau of the Census, 1993].

Piedmont and Coastal Plain watersheds differ markedly in their discharge characteristics. Discharge of nitrogen species increases with proportion of cropland in both provinces, but discharges of nitrate and total nitrogen from Piedmont watersheds greatly exceed discharges from Coastal Plain watersheds with similar proportions of cropland [Jordan et al., 1997a, b]. Discharges of particulate matter, phosphorus species, organic carbon, and dissolved silica differ greatly among watersheds but do not correlate with the proportion of cropland [Jordan et

al., 1997a, b]. This study investigates the interactive effects of land use and streamflow characteristics on discharges of organic carbon, dissolved silica, and various forms of nitrogen and phosphorus from 27 watersheds, of which 17 are in the Coastal Plain and 10 are in the Piedmont.

2. Methods

2.1. Study Watersheds

To reduce the number of confounding factors, we selected study watersheds that have differing proportions of agricultural and nonagricultural land, low populations of humans, and no sewage outfalls, reservoirs, or lakes. The 17 Coastal Plain watersheds were distributed in four clusters in the Chesapeake drainage (Figure 1). One cluster, which we have studied for over 20 years [e.g., Correll, 1977, 1987; Jordan et al., 1986a, 1991a], included seven inner Coastal Plain watersheds in the drainage of the Rhode River (101–111; see Figure 1), a small subestuary on the western shore of the Chesapeake. Another cluster, also on the inner Coastal Plain (301–303), was at the northern end of the Delmarva Peninsula. A cluster on the central Coastal Plain (304–306, 310) was in an area of high-intensity corn, wheat, and soybean farming, and a cluster on the outer Coastal Plain (307–309) was in an area of intensive poultry farming. The Coastal Plain watersheds were mostly 100–2000 ha in area and were 0–67% cropland (Table 1). The

10 Piedmont watersheds (401–410) we studied were located along the Pennsylvania-Maryland border north of Baltimore, Maryland (Figure 1). The Piedmont watersheds were 53–3200 ha in area and were composed of 0–60% cropland (Table 1). Areas of the different land types were measured from 1:9600 scale color-infrared aerial photographs taken within 2 years of the study by the National Aerial Photography Program [U.S. Geological Survey, 1991]. The identity of cropland, which can resemble grassland in aerial photographs, was confirmed by examining all the fields on the ground.

2.2. Sampling

We used automated samplers to monitor discharges of water, nutrients, and suspended solids from the streams that drain the study watersheds [Jordan et al., 1997a, b]. Automation ensures adequate sampling of particulate fractions in storm flow [Jordan et al., 1986b]. At the Rhode River site, samplers measure flow with V-notch weirs and pump samples after a set amount of flow [Correll, 1977, 1981]. At other sites, the samplers monitored stream depth and calculated water flow from rating curves of flow versus depth. Each of these samplers had a Campbell CR10 data logger that recorded depth, calculated flow, and controlled a pump to collect samples of stream water after a set amount of flow had occurred. Thus samples were pumped more frequently at higher flow rates, up to once every 5 min during storm flow. Samples were pumped from the middle of the stream through plastic tubing that was first rinsed with stream water. Two sets of flow-weighted composite samples, one with sulfuric acid as a preservative, were collected each week for analysis. The composition of these samples is representative of total discharge from overland storm flow and from groundwater emerging in the stream. The sampling reported here covered a 1-year period from December 1990 through November 1991 when all watersheds were studied concurrently.

2.3. Chemical Analyses

Details of chemical analyses are given by Jordan et al. [1997a, b]. Briefly, N, P, and organic C were analyzed in acid-preserved samples using the following techniques. Phosphate (PO₄) was analyzed by reaction with stannous chloride and ammonium molybdate [American Public Health Association (APHA), 1989], total P (TP) was measured using a perchloric acid digestion [King, 1932], ammonium (NH₄) was measured by oxidation to nitrite [Strickland and Parsons, 1972], the sum of organic N and NH₄-N was determined using the Kjeldahl digestion [Martin, 1972; APHA, 1989], the sum of nitrite and nitrate (NO₃) was analyzed by cadmium reduction [APHA, 1989], and total organic carbon (TOC) was analyzed by reaction with potassium dichromate [Maciolek, 1962; Gaudy and Ramanathan, 1964]. PO₄ and NH₄ measured in acid-preserved samples represent the total of dissolved and acid-extractable forms. Total organic P (TOP) was calculated by subtracting PO₄ from TP. Total organic N (TON) was calculated by subtracting NH₄ from total Kjeldahl N.

We measured concentrations of suspended solids and dissolved silica in the unpreserved composite samples. Suspended solids were collected on preweighed 0.45-μm membrane filters which were dried and reweighed. Dissolved silica was analyzed in 0.45-μm filtered samples with a Technicon Auto-Analyzer II (method 696-82W).

Table 1. Total Areas and Percentages of Land Use Types for Study Watersheds

Watershed	Area, ha	Land Use, %		
		Cropland	Forest	Other
<i>Inner Coastal Plain (Rhode River)</i>				
101	226	2.3	52.4	45.3
102	193	6.2	59.6	34.2
103	247	1.7	71.0	27.3
108	150	26.3	51.6	22.1
109	17.0	60.2	34.6	5.2
110	6.2	0	98.2	1.8
111	5.5	0	11.3	88.7
<i>Inner Coastal Plain (Delmarva)</i>				
301	569	0.3	98.3	1.4
302	971	28.1	50.6	21.3
303	478	15.0	25.3	59.7
<i>Central Coastal Plain</i>				
304	1077	66.3	30.4	3.3
305	1757	59.8	28.8	11.4
306	684	66.7	28.3	5.0
310	5240	67.0	27.0	6.0
<i>Outer Coastal Plain</i>				
307	139	1.3	88.8	9.9
308	1241	45.6	52.0	2.4
309	1632	41.3	56.9	1.8
<i>Piedmont</i>				
401	117	0	97.7	2.3
402	596	34.2	42.3	23.5
403	3220	41.6	28.3	30.1
404	350	60.3	9.77	29.9
405	611	38.8	29.7	31.5
406	552	21.6	68.0	10.4
407	53.3	0	84.2	15.8
408	799	58.3	21.6	20.1
409	376	50.2	34.4	15.4
410	820	49.5	27.8	22.7

From Jordan et al. [1997a, b].

2.4. Base Flow Index

The proportion of water discharged as base flow was estimated from daily flow rates using an algorithm that implements an operational definition of base flow [Gustard et al., 1992]. The calculation of the base flow index proceeds as follows:

1. Divide daily flow into nonoverlapping blocks of 5 days and find the minimum for each block.
2. Compare each block minimum in the series with those before and after it. If 0.9 times the minimum is less than both of the neighboring block minima, then it is considered a measurement of base flow.
3. Estimate the base flow for each day by linear interpolation between 5-day block minima that were classified as base flow measurements.
4. If the estimated base flow for a particular day is greater than the total measured flow, then redefine the estimated base flow to be the measured flow.
5. Calculate the base flow index for the whole series (in our case, 1 year) as the sum of the daily estimated base flows divided by the sum of daily measured flows.

3. Results

Base flow index differed greatly among watersheds. A comparison of two similar-sized Coastal Plain watersheds that re-

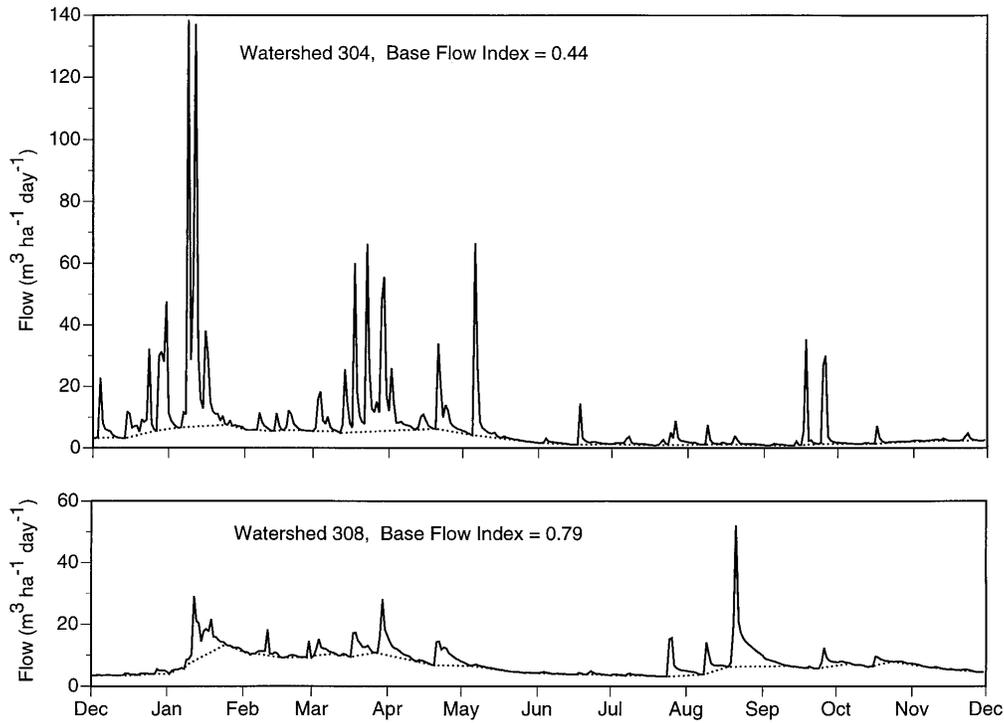


Figure 2. Daily flow (solid line) and base flow (dotted line) from watershed 304 in the central Coastal Plain and watershed 308 in the outer Coastal Plain from December 1990 to November 1991. Base flow was derived by the smoothed minima technique [Gustard *et al.*, 1992]. The area under the dotted line is annual base flow. The area under the solid line is total annual flow. The base flow index is the annual base flow divided by the annual total flow.

leased similar amounts of water illustrates the differences (Figure 2). Water flow from watershed 304, having a base flow index of 0.44, was clearly dominated by brief episodes of high discharge, while water flow from watershed 308, having a base flow index of 0.79, was much more constant through time. In both of these watersheds and in others we studied, base flow was highest in late winter and early spring when aquifers were recharged and evapotranspiration was low (Figure 2). However, base flow was obviously a more important component of the total flow for watershed 308 than for watershed 304. In general, water flow from Piedmont watersheds was dominated by base flow, while flow from Coastal Plain watersheds was usually dominated by episodes of high flow. Thus base flow indices were generally higher for Piedmont watersheds than for Coastal Plain watersheds (Figure 3). Base flow indices for all Piedmont watersheds were above 0.5, while indices for 80% of the Coastal Plain watersheds were below 0.5 (Figure 3).

Another striking difference between Piedmont and Coastal Plain watersheds is in the concentration of NO_3 in their discharges. In both provinces, annual flow-weighted mean NO_3 concentrations increase as the proportion of cropland in the watershed increases, but in the Piedmont the rate of increase is much greater (Figure 4). At any given percentage of cropland, NO_3 concentrations for Piedmont watersheds were generally more than double those for Coastal Plain watersheds (Figure 4).

Can the differences in NO_3 concentrations between provinces be attributed to differences in the proportions of base flow? Unusual NO_3 concentrations for watersheds with un-

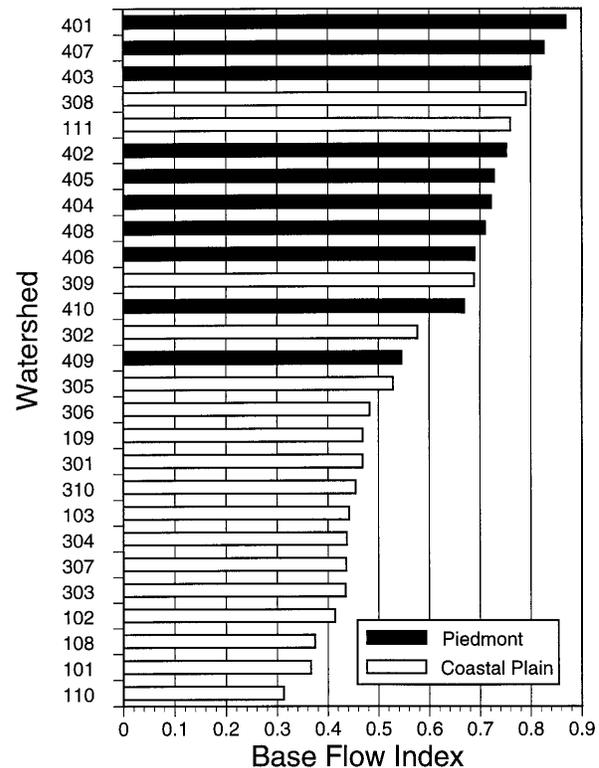


Figure 3. Base flow index calculated according to Gustard *et al.* [1992] for Piedmont and Coastal Plain watersheds.

usual base flow indices suggest so. For example, Coastal Plain watersheds 308 and 309 had unusually high base flow indices and high NO₃ concentrations compared with other Coastal Plain watersheds (Figures 3 and 4), while Piedmont watersheds 409 and 410 had unusually low base flow indices and low NO₃ concentrations compared with other Piedmont watersheds. We can distinguish the effects of base flow from the other effects related to province because there were differences in base flow indices among watersheds within provinces and the ranges of base flow indices for the two provinces overlapped (Figure 3).

We used a general linear model to test the effects of cropland, base flow index, and province on NO₃ concentration. Cropland and base flow index were continuous variables, and province was a classification variable. The interaction of cropland and base flow index was incorporated using the cross product term cropland × baseflow, which lets the linear effect of cropland change linearly with base flow index (or vice versa). Interactions of cropland and base flow index with province were also included. We tested the individual variables and their interactions in the following order: cropland, base flow index, cropland × base flow index, province, cropland × province, base flow × province, and cropland × base flow × province. The significance of each term in the model was tested after accounting for the effects of the previous terms. Cropland and base flow were entered first because of their mechanistic implications. The classification variable “province” and its interactions were tested after accounting for cropland, base flow, and their cross product to see if other, unspecified differences between the provinces might account for some of the variance not linked to the direct or interacting effects of cropland and base flow.

The effects of cropland and base flow index and their interaction were highly significant in predicting NO₃ concentrations (Table 2). A model with these three terms explains 79% of the variance (85%, if watershed 407 data are omitted; see Table 2). After accounting for these mechanistic effects, there was still a significant effect of the classification variable “province,”

Table 2. Statistical Significance *p* and Percentage of Variance Explained for Linear Models Relating Flow-Weighted Mean Concentrations of NO₃ to the Percentage of Cropland in the Watershed, the Base Flow Index, and the Province (Piedmont or Coastal Plain)

Model Term	Without 407		With 407	
	Variance Explained, %	<i>p</i>	Variance Explained, %	<i>p</i>
Percentage of cropland	51	0.0001	45	0.0001
Base flow index	69	0.0013	68	0.0003
Crop × base flow	85	0.0001	79	0.0019
Province	89	0.0085	86	0.0056
Crop × province	91	0.073	86	0.49
Base flow × province	93	0.065	87	0.13
Crop × base flow province	93	0.53	88	0.42

Each *p* value is for a particular model term. Each percentage of variance explained is for a model including the term on the line and all terms on previous lines. For all models that include terms on previous lines, *p* < 0.0001. Results are shown for models with and without the data from watershed 407, where NO₃ concentration was anomalously high.

which explained an additional 4–7% of the variance (Table 2). However the effects of interactions of other variables with province were not significant. Similar results were obtained whether or not we omitted the anomalous NO₃ data from watershed 407 (Table 2). Watershed 407 was an almost entirely forested watershed but discharged unusually high amounts of NO₃ (Figure 4). Because of this and the small size of the watershed (Table 1), it seems likely that the watershed receives inputs from aquifers outside of the surface drainage boundaries that we used to define the watershed area [Jordan et al., 1997b].

The model for predicting NO₃ concentration can be simplified by omitting the nonsignificant interactions with province from the full statistical model (Table 2). The simplified model explains 86–89% of the variability in NO₃ concentration with or without the anomalous watershed 407. The model predicts that NO₃ concentrations increase as the percentage of cropland increases but that the rate of increase is greater for watersheds having higher base flow indices (Figure 5). The significant effect of province indicates that NO₃ concentrations at given percentages of cropland and given base flow indices are significantly lower for Coastal Plain watersheds than for Piedmont watersheds (Figure 5). The magnitude of this effect does not vary with cropland or base flow index because their interactions with province were not significant. According to our model, NO₃ concentrations increase as the base flow index increases when the percentage of cropland is above 10%, while at less than 10% cropland, NO₃ concentrations decrease slightly as base flow index increases (Figure 5). Measured NO₃ concentrations for watersheds with less than 10% cropland do not show the predicted decrease with increasing base flow index. However, measured concentrations generally corresponded well with concentrations predicted by the model, except for Piedmont watersheds 404 and 407, which had unexpectedly high concentrations (Figure 6).

We also found significant correlations between base flow index and concentrations of TON and TOC. Applying the same linear model as we used for NO₃ concentrations, we found the individual effects of cropland and base flow index to

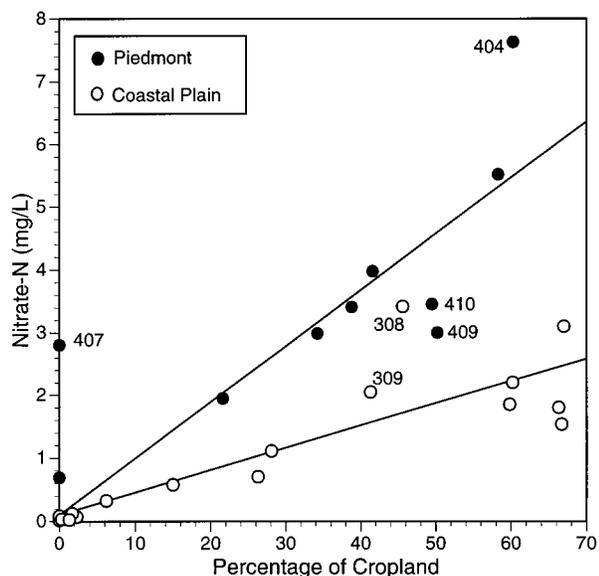


Figure 4. Annual flow-weighted mean concentration of NO₃ versus the percentage of cropland in watersheds of the Piedmont [Jordan et al., 1997b] and Coastal Plain [Jordan et al., 1997a]. Watershed numbers are indicated for outlying data.

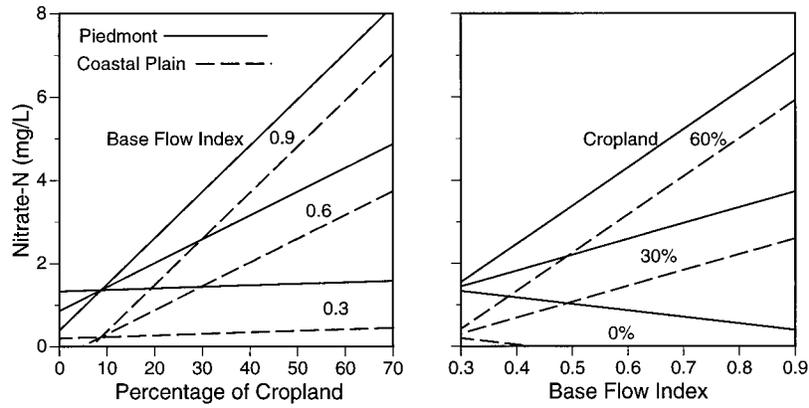


Figure 5. Predicted NO_3 concentrations (left) versus the percentage of cropland and (right) versus base flow index. Different lines for different base flow indices and percentages of cropland are shown. Solid lines are for Piedmont watersheds and dashed lines for Coastal Plain watersheds. Concentrations are predicted from a statistical model based on the percentage of cropland (c), the base flow index (b), the interaction of c and b , and the province: for the Piedmont, $\text{NO}_3 = 1.796 - 0.0501c - 1.561b + 0.1796cb$; for the Coastal Plain, $\text{NO}_3 = \text{Piedmont NO}_3 - 1.132$. The anomalous concentration from watershed 407 was omitted in fitting the model. Other details about the model are given in Table 2.

be highly significant for TON, explaining 52% of the variance together (Table 3). For TOC, only the effect of base flow index was significant (Table 3), explaining 49% of the variance by itself. No differences in TON or TOC could be attributed to the effect of province after accounting for the effects of cropland and base flow index, nor were any interactions significant (Table 3). Changing the order in which terms were added into the model did not alter the conclusions.

In contrast to NO_3 , TON concentrations decreased as the proportion of base flow increased, regardless of the percentage of cropland in the watershed. Like NO_3 , TON concentrations increased as the percentage of cropland increased (Figure 7). Predicted TON concentrations corresponded well with measured concentrations and were not unusually discrepant for any particular watershed (Figure 6).

Like TON, TOC concentration decreased linearly as base flow index increased (Figure 8). The relationship appeared the

same regardless of province or percentage of cropland, and none of the watersheds stood out as outliers (Figure 8).

Concentrations of total NH_4 , total PO_4 , TOP, TP, and suspended solids did not show significant correlations with base flow index. Concentrations of P species and suspended solids did not correlate with percentages of cropland. However, total NH_4 concentration increased with the percentage of cropland for Coastal Plain watersheds ($r^2 = 0.273$, $p = 0.031$). Also, for Coastal Plain watersheds, concentrations of P species correlated with the concentration of suspended solids ($p < 0.0001$). Similarly, for Piedmont watersheds, TOP concentrations correlated with suspended solids ($p = 0.023$), although other forms of P did not. For Coastal Plain watersheds, total P concentration was approximately equal to 0.005 times the concentration of suspended solids (Figure 9). Some of the Piedmont watersheds seem to follow this relationship, but most have less total P than would be predicted from the relationship

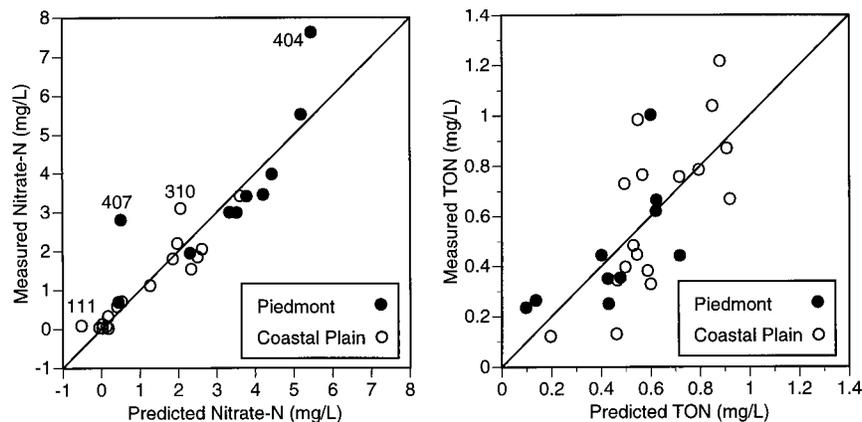


Figure 6. (left) Measured annual flow-weighted mean concentration of NO_3 versus the concentration predicted from the statistical model (Figure 5) for Piedmont and Coastal Plain watersheds. Watershed numbers are indicated for outlying data. (right) Measured annual flow-weighted mean concentration of TON versus the concentration predicted from the statistical model (Figure 7) for Piedmont (solid circles) and Coastal Plain (open circles) watersheds. For both panels, measured and predicted concentrations are equal along the solid line. Measured concentrations for the Coastal Plain and Piedmont are from Jordan *et al.* [1997a] and Jordan *et al.* [1997b], respectively.

Table 3. Statistical Significance *p* and Percentage of Variance Explained for Linear Models Relating Flow-Weighted Mean Concentrations of Total Organic Nitrogen and Total Organic Carbon to the Percentage of Cropland in the Watershed, the Base Flow Index, and the Province (Piedmont or Coastal Plain)

Model Term	TON		TOC	
	Variance Explained, %	<i>p</i>	Variance Explained, %	<i>p</i>
Percentage of cropland	26	0.0061	1.3	0.57
Base flow index	52	0.0016	52	0.0001
Crop × base flow	53	0.57	53	0.54
Province	53	0.70	57	0.13
Crop × province	53	0.63	60	0.24
Base flow × province	54	0.55	62	0.41
Crop × base flow × province	54	0.83	62	0.56

Each *p* value is for a particular model term. Each percentage of variance explained is for a model including the term on the line and all terms on previous lines. For all models that include terms on previous lines, *p* < 0.02.

to suspended solids in the Coastal Plain (Figure 9). This may be due to a higher P content of suspended solids discharged from the Coastal Plain watersheds compared to those discharged from the Piedmont watersheds.

Since the concentrations of N and P species correlate with different factors, the ratio of N to P in watershed discharges differs widely among watersheds. Atomic N:P ratios were lowest for the inner Coastal Plain watersheds of the Rhode River, where they ranged from 6.4 to 11, and highest for the outer Coastal Plain and the Piedmont, where they ranged from 28 to 200 (Table 4).

Concentrations of dissolved silica did not correlate with land use or base flow index but differed among watershed clusters. Concentrations were lowest for the Delmarva inner Coastal Plain and for the Piedmont, where they ranged from 1.9 to 5.2 mg/L (Table 4). Elsewhere, dissolved silica concentrations ranged up to 9.9 mg/L (Table 4).

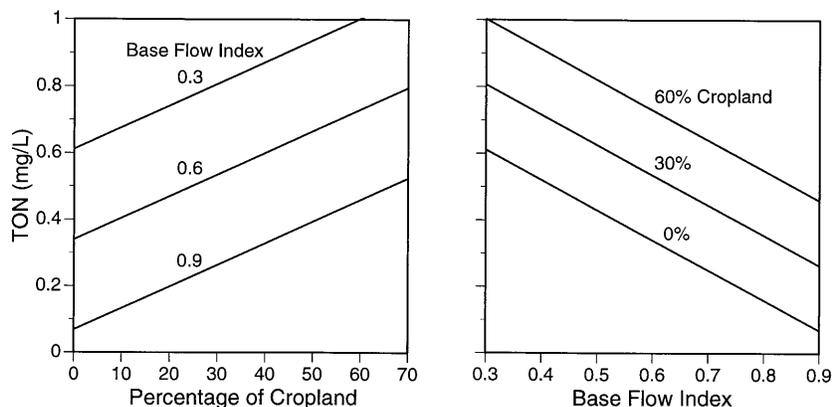


Figure 7. Predicted TON concentrations (left) versus the percentage of cropland and (right) versus base flow index. Different lines for different base flow indices and percentages of cropland are shown. Concentrations are calculated from a statistical model based on the percentage of cropland (*c*) and the base flow index (*b*): $TON = 0.883 + 0.00652c - 0.905b$. Other details about the model are given in Table 3.

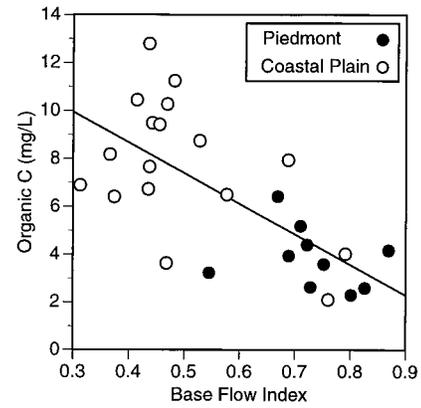


Figure 8. Annual flow-weighted mean concentration of TOC versus the base flow index for Piedmont and Coastal Plain watersheds. The line was fit by linear regression (*p* < 0.001, $r^2 = 0.49$). TOC concentrations for the Coastal Plain and Piedmont are from *Jordan et al.* [1997a] and *Jordan et al.* [1997b], respectively.

4. Discussion

Base flow can be defined as “the rate at which a groundwater store discharges in the absence of recharge” [*Nathan and McMahon, 1990, p. 1465*]. Many techniques have been developed to estimate base flow from hydrographs [*Nathan and McMahon, 1990; Gustard et al., 1992*]. All these techniques are somewhat arbitrary and are based on operational definitions of base flow because it is impossible to know the base flow component of the total flow during recharge events. We chose a smoothed minima technique for estimating base flow [*Gustard et al., 1992*] because of its simplicity and lack of assumptions. Other techniques would yield different estimates of base flow but similar rankings of the proportions of base flow from different watersheds [e.g., *Nathan and McMahon, 1990*]. Therefore we stress that the base flow index we used is not an absolute measurement of the proportion of groundwater discharge but that it would correlate with the proportion of groundwater discharge among watersheds.

Our statistical models based on the proportion of cropland

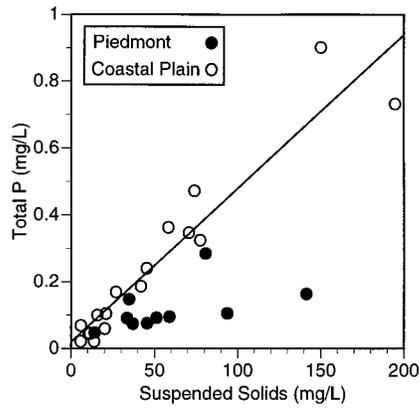


Figure 9. Annual flow-weighted mean concentration of total P versus the annual flow-weighted mean concentration of total suspended solids for watersheds in the Piedmont [Jordan *et al.*, 1997b] and Coastal Plain [Jordan *et al.*, 1997a]. The regression line is shown for Coastal Plain data ($p < 0.001$, $r^2 = 0.90$).

and the base flow index explain 54–93% of the variance in concentrations of different forms of N and organic C (Tables 2 and 3). Thus nonpoint source discharges of these nutrients from Piedmont and Coastal Plain watersheds other than those we studied could be predicted from measurements of water flow rates [e.g., Darling, 1962], the base flow index, and the extent of cropland. Unfortunately, the extent of cropland is often poorly known because land use inventories that are based on remote sensing are poor at distinguishing cropland from grassland [e.g., *Environmental Monitoring and Assessment Program*, 1994]. Ground-based observations, such as we used to identify cropland, are practical only for relatively small areas. For areas the size of counties or larger, agricultural statistics for counties [e.g., *Bureau of the Census*, 1993] can provide measurements of cropland areas, but there is clearly a need for more accurate mapping of cropland. Characteristic base flow indices for different regions can be calculated from data on daily stream flow, but only for watersheds without lakes or reservoirs that would affect the evenness of stream flow. In addition, the predictive ability of our models should be verified by comparing predicted and measured nutrient concentrations for other watersheds.

Annual nutrient discharge can be calculated by multiplying the predicted annual flow-weighted mean concentrations by the annual water flow. Water flow during our 1-year study was below the long-term mean flow for streams near our watersheds, probably because rainfall was below average during the study [Jordan *et al.*, 1997a, b; Darling, 1962]. Also, water flow per hectare decreased as area decreased for Coastal Plain watersheds of less than 700 ha [Jordan *et al.*, 1997a]. Therefore to obtain an estimate of nutrient discharge that is representative of large basins during average rainfall conditions, it is better to multiply concentrations by long-term regional mean water flows rather than by water flows measured from our study watersheds. Regional mean water flows were about 45 cm yr^{-1} for inner Coastal Plain watersheds, 35 cm yr^{-1} for central and outer Coastal Plain watersheds, and 42 cm yr^{-1} for Piedmont watersheds [Jordan *et al.*, 1997a, b; Darling, 1962]. Differences in water flows affect nutrient discharges, but these differences are small in comparison with the differences in nutrient concentrations among watersheds. However, future studies would be needed to confirm that differences in annual

water flow do not cause significant differences in annual mean nutrient concentrations.

In addition to predicting nutrient concentrations, our models also suggest the underlying mechanisms that control nutrient discharges. Increases in N discharge with increasing proportions of cropland have commonly been observed [e.g., Omernik, 1976; Beaulac and Reckhow, 1982; Rekolainen, 1990; Frink, 1991; Correll *et al.*, 1992] and are probably related to N applications to cropland. However, the correlations with base flow index suggest that the way water flows over and through the soil also affects discharges. Water flow from a watershed having a high base flow index is predominantly through groundwater emerging in streams, while flow from a watershed having a low base flow index is predominantly surface runoff or shallow subsurface flow. Thus the increase in concentrations of organic N and C with decrease in base flow index suggests that these organic nutrients are transported mainly in surface runoff and shallow subsurface flow. Conversely, the increase in NO_3 concentration with increase in base flow index suggests that nitrate is transported mainly in groundwater flow. These deductions are consistent with other findings. Gambrell *et al.* [1975] compared N fluxes in poorly drained and moderately well drained cornfield soils and found that organic N was mainly transported in surface runoff, which was higher for poorly drained than for well-drained soils. They also found

Table 4. Annual Flow-Weighted Mean Concentrations of Dissolved Silica, Total N, and Total P, and Atomic N:P Ratios in Discharges From the Study Watersheds

Watershed	Silica-Si, mg L^{-1}	Total N, mg L^{-1}	Total P, mg L^{-1}	Atomic N:P
<i>Inner Coastal Plain (Rhode River)</i>				
101	6.0	1.0	0.35	6.4
102	5.4	1.5	0.47	7.1
103	9.9	0.94	0.73	2.8
108	9.5	1.7	0.32	11
109	9.4	3.6	0.90	8.9
110	5.2	0.48	0.10	11
111	...	0.25	0.068	8.0
<i>Inner Coastal Plain (Delmarva)</i>				
301	3.0	0.19	0.021	21
302	4.0	1.6	0.059	62
303	4.4	1.1	0.10	23
<i>Central Coastal Plain</i>				
304	6.8	2.6	0.17	34
305	6.0	2.8	0.19	33
306	6.8	3.1	0.36	19
310	6.1	4.1	0.24	38
<i>Outer Coastal Plain</i>				
307	3.4	0.52	0.021	55
308	6.5	3.8	0.044	190
309	7.8	2.6	0.046	120
<i>Piedmont</i>				
401	3.4	0.95	0.075	28
402	4.6	3.4	0.095	79
403	2.6	4.3	0.047	200
404	2.6	8.4	0.15	130
405	2.6	3.8	0.090	94
406	3.0	2.4	0.10	51
407	5.2	3.1	0.073	94
408	2.8	6.2	0.16	85
409	1.9	3.5	0.091	85
410	2.7	4.7	0.28	36

From Jordan *et al.* [1997a, b].

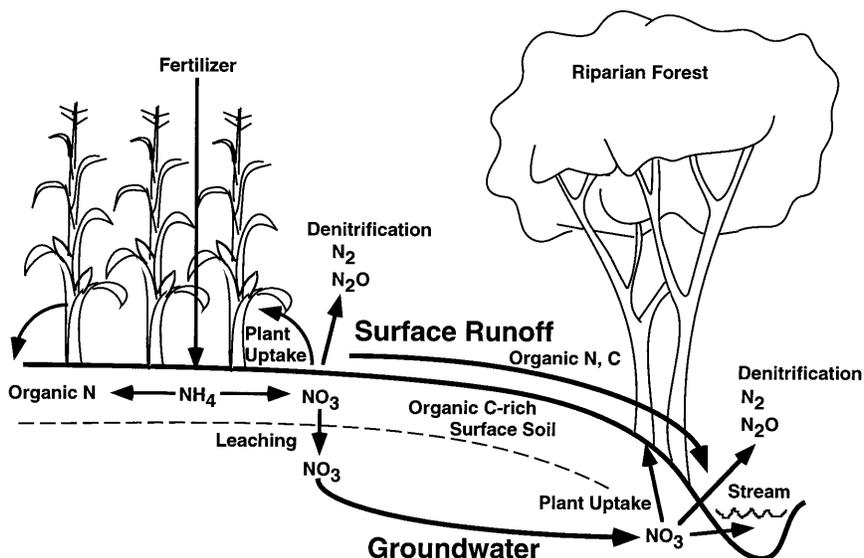


Figure 10. Conceptual model of the transport of NO_3 via groundwater flow, and organic N and C via surface runoff.

much greater transport of NO_3 through subsurface drainage in the well-drained soils and hypothesized that more NO_3 was lost through denitrification in the poorly drained soils. Similarly, *Groffman et al.* [1992] found that denitrification rates in forest soils are greater in finer-textured soils, and *Dillon et al.* [1991] found that organic N discharge from forested watersheds increases as the proportion of “quick flow” increases. *Brenner and Mondok* [1995] found that NO_3 discharge rate was greater for watersheds having soil and aquifer characteristics favoring infiltration and subsurface flow. *Kronvang et al.* [1995] derived a multiple-regression model to predict nutrient discharges from several watershed characteristics including the proportions of arable land and the proportions of soil types of different permeabilities.

It is surprising that the discharges of suspended solids and P were not related to the base flow index. One would expect that watersheds with a predominance of surface runoff would discharge greater amounts of suspended solids and associated P. Greater predominance of surface runoff should correlate with lower base flow indices, although some nonbase flow may be shallow subsurface flow. Transport of suspended solids may be more related to the erodibility of soil particles than to the proportion of surface runoff. P transport would be affected both by the transport and by the P content of the suspended solids. Other studies report that discharges of P are affected by the geochemistry of the soils in the watershed [*Dillon and Kirchner*, 1975; *Grobler and Silberbauer*, 1985; *Rekolainen*, 1990; *Vighi et al.*, 1991]. Differences in the P geochemistry of soils in different provinces could account for the differences we observed in the relationships between concentrations of suspended solids and total P (Figure 9).

The lack of correlation between base flow and suspended solids indicates that the correlations of between base flow and organic N and C are not due to an increase in transport of particulate matter with increased surface runoff. This is consistent with previous findings that most of the organic N and C is in dissolved form. Separate analyses of dissolved and particulate fractions in discharges from our watersheds indicate that dissolved organic N and C averaged 70–80% of the total or-

ganic N and C, except in the Rhode River watersheds where dissolved organic N averaged 38% of the total organic N and dissolved organic C averaged 50% of the total organic C [*Jordan et al.*, 1997a, b].

Even after accounting for the proportion of cropland and the base flow index, there is still a systematic difference in NO_3 discharge between Piedmont and Coastal Plain watersheds. Coastal Plain watersheds discharge less NO_3 per hectare than Piedmont watersheds having similar proportions of cropland and similar base flow indices (Figure 5). The difference is apparently not due to differences in anthropogenic N inputs, because inputs of N per hectare of cropland are about the same for most of the watersheds we studied [*Jordan et al.*, 1997a, b]. However, NO_3 discharges from Coastal Plain watersheds may be reduced by uptake of NO_3 in riparian forests. On the Coastal Plain, agricultural fields are typically located on well-drained uplands above poorly drained riparian forests [*Gilliam and Skaggs*, 1988; *Correll*, 1991] that can retain 70–90% of the total N inputs entering mainly as NO_3 in subsurface discharges from adjacent cropland [*Lowrance et al.*, 1984, 1985; *Peterjohn and Correll*, 1984; *Jacobs and Gilliam*, 1985; *Peterjohn and Correll*, 1986; *Jordan et al.*, 1993]. NO_3 retention in riparian forests may be due to either plant uptake or denitrification [*Lowrance et al.*, 1984; *Peterjohn and Correll*, 1984; *Jacobs and Gilliam*, 1985; *Lowrance*, 1992; *Haycock and Pinay*, 1993]. It is not known whether riparian forests in the Piedmont can intercept NO_3 as effectively as can those in the Coastal Plain [*Lowrance et al.*, 1995]. Groundwater flow patterns in the Piedmont may not be as favorable as those in the Coastal Plain for NO_3 uptake in riparian zones. In the Coastal Plain, layers of impermeable sediment can force groundwater flow near the soil surface in riparian zones, enhancing the potential for denitrification and N uptake by plants [*Jordan et al.*, 1993]. In the Piedmont, groundwater may flow deeper, passing through fractured regolith as much as 30 m beneath the riparian soils [*Pavich et al.*, 1989] to emerge in the stream, with less possibility of NO_3 interception within the riparian zone. Also, in the Piedmont, less of the forest is riparian than in the Coastal Plain. In fact, much of the forest in our Piedmont watersheds

is on hilltops, where the soil is too dry and rocky for crops, and much of the riparian zone is used for pasture.

Characteristics of riparian zones have been used as predictive variables in some statistical models of watershed discharge [Omerik *et al.*, 1981; Osborne and Wiley, 1988; Hunsaker and Levine, 1995; Johnson *et al.*, 1997]. However, in some cases, there was no significant relationship between nutrient discharge and riparian zone characteristics [Omerik *et al.*, 1981; Hunsaker and Levine, 1995]. This may reflect variability in the nutrient trapping efficiency of riparian zones.

The N, P, dissolved Si, and TOC discharged by watersheds contribute to eutrophication of receiving waters. N and P were discharged in widely different proportions by different types of watersheds, but for all except the Rhode River watersheds, the atomic N:P ratios discharged were higher than 16 (Table 4), the typical N:P ratio in phytoplankton biomass [Redfield, 1958]. This suggests that the discharges would promote P limitation of phytoplankton growth in the receiving waters. High atomic N:P ratios have also been found in discharges from major tributaries to the Chesapeake Bay, the Potomac River (N:P = 23 [Jaworski *et al.*, 1992]) and the Susquehanna River (N:P = 66 [Ott *et al.*, 1991]). Dissolved silica concentrations in discharges from the Coastal Plain were generally higher than in discharges from the Piedmont (Table 4), suggesting that Coastal Plain discharges could support more diatom growth than could Piedmont discharges.

Increase in N discharge with increase in the proportion of cropland in the watershed probably results from anthropogenic inputs of N to croplands. However, our study suggests that hydrological properties of the watershed strongly influence the proportion of the anthropogenic input that is discharged (Figure 10). We hypothesize that the main path of N discharge is via downward leaching of NO₃ out of the rooting zone and into groundwater that later emerges in streams. Thus in watersheds having higher base flow indices, indicating greater predominance of infiltration over surface runoff, more NO₃ will be leached from the surface soils and carried to the stream in shallow groundwater. In watersheds having lower base flow indices, indicating less infiltration, more NO₃ will be held in the surface soils, where it can be taken up by plants or denitrified. We further hypothesize that organic N and C are less prone to leaching than NO₃ and thus are transported more effectively by surface runoff, which predominates in watersheds with low base flow indices. NO₃ transport through groundwater to streams may be reduced by interception in riparian forests, especially in the Coastal Plain. Our study suggests that the partitioning of water flow between surface runoff and shallow groundwater is of overriding importance in determining nutrient discharges. Moreover, this partitioning is well characterized by a very simple integrative measurement, the base flow index.

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