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NONPOINT SOURCE DISCHARGES OF NUTRIENTS FROM PIEDMONT WATERSHEDS OF CHESAPEAKE BAY[1]

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ABSTRACT: We measured annual discharges of water, sediments, and nutrients from 10 watersheds with differing proportions of agricultural lands in the Piedmont physiographic province of the Chesapeake Bay drainage. Flow-weighted mean concentrations of total N, nitrate, and dissolved silicate in watershed discharges were correlated with the proportion of cropland in the watershed. In contrast, concentrations of P species did not correlate with cropland. Organic P and C correlated with the concentration of suspended particles, which differed among watersheds. Thus, the ratio of N:P:Si in discharges differed greatly among watersheds, potentially affecting N, P or Si limitation of phytoplankton growth in the receiving waters. Simple regression models of N discharge versus the percentage of cropland suggest that croplands discharge 29-42 kg N ha^{-1} yr^{-1} and other lands discharge 1.2-5.8 kg N ha^{-1} yr^{-1}. We estimated net anthropogenic input of N to croplands and other lands using county level data on agriculture and N deposition from the atmosphere. For most of the study watersheds, N discharge amounted to less than half of the net anthropogenic N.
(KEY TERMS: nonpoint source pollution; nutrients; water quality; agriculture; watersheds; Chesapeake Bay.)

INTRODUCTION

Anthropogenic increases in nonpoint source nutrient releases have led to the accelerated eutrophication of estuaries throughout the world (Nixon, 1995). For Chesapeake Bay, one of the world's largest estuaries, nonpoint source discharges from the watershed contribute approximately two-thirds of the nitrogen, one-quarter of the phosphorus, and all of the silicate inputs (Correll, 1987). Nitrogen and phosphorus loads to the Chesapeake Bay watershed come mostly from agriculture, but atmospheric deposition is also an important source of nitrogen. Recent estimates suggest that 40 percent of the nitrogen load to the Chesapeake Bay watershed comes from atmospheric deposition, 33 percent from livestock waste, and 27 percent from fertilizer (Fisher and Oppenheimer, 1991). Similarly, a study of the upper Potomac River basin, a major subwatershed of Chesapeake Bay, found that 28 percent of the nitrogen load to the watershed comes from atmospheric deposition, 12 percent from biotic fixation and adsorption on surfaces of leaves, 16 percent from fertilizer, and 44 percent from animal waste (Jaworski *et al.*, 1992). By comparison, only 8.2 percent of the phosphorus load to the upper Potomac River basin comes from atmospheric deposition, while 30 percent comes from fertilizer, and 62 percent from animal waste (Lugbill, 1990).

Anthropogenic increases in watershed inputs of both nitrogen and phosphorus to Chesapeake Bay have led to excessive plankton production (Malone *et al.*, 1986, 1988; Boynton *et al.*, 1982; Correll, 1987; Jordan *et al.*, 1991a,b; Gallegos *et al.*, 1992). This has contributed to the demise of submerged aquatic vegetation (Kemp *et al.*, 1983) and the increase in the extent of hypoxic waters (Taft *et al.*, 1980; Officer *et al.*, 1984). Elevated nitrogen and phosphorus inputs have also led to seasonal depletion of dissolved silicate, resulting in altered phytoplankton production and species composition in the middle to lower Bay (D'Elia *et al.*, 1983; Anderson, 1986; Conley and Malone, 1992).

The 178,000 km^2 watershed of Chesapeake Bay extends over three physiographic regions: the Coastal Plain, the Piedmont, and the Appalachian, which differ in land use patterns, topography, hydrology, and

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geology. About 23 percent of the Chesapeake watershed is in the Piedmont (NCRI Chesapeake, 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 percent of the agricultural land in the Chesapeake watershed (NCRI Chesapeake, 1982). The main crops are corn, soybeans, alfalfa, and wheat, and livestock production is mainly dairy (Bureau of the Census, 1993).

The objective of this study is to test the effects of agricultural land use on discharges of water, sediments, and nutrients from Piedmont watersheds of the Chesapeake Bay. Our approach is to compare annual discharges from 10 watersheds that have differing proportions of agricultural lands. We also calculate the net anthropogenic input of N to these watersheds to test the hypothesis that N discharges are correlated with anthropogenic inputs. Finally, we compare the results of this study of Piedmont watersheds to results of a similar study of Coastal Plain watersheds (Jordan *et al.*, in press) to test whether the relationships of inputs with discharges differ between physiographic provinces.

METHODS

Study Watersheds

We studied 10 Piedmont watersheds located along the Pennsylvania-Maryland border north of Baltimore, Maryland (Figure 1) in an area underlain by silicaceous metamorphic rock. We selected watersheds with differing proportions of agricultural and nonagricultural land, low populations of humans, and no sewage outfalls. The watersheds were between 53 ha and 3200 ha in area and were composed of 0-60 percent cropland, 10-98 percent forest, and 2-30 percent other land types (Table 1). Areas of the different land types were measured from 1:9600 scale color-infrared aerial photographs taken within two years of the study by the USDA-ASCS (NAPP, 1991). The identity of cropland, which can resemble pasture in aerial photographs, was confirmed by observations on the ground.

Flow Measurements and Sampling

We used automated samplers to monitor discharges of water, nutrients, and sediments from the streams that drain the study watersheds. The automated samplers monitored depth in the stream channel with a

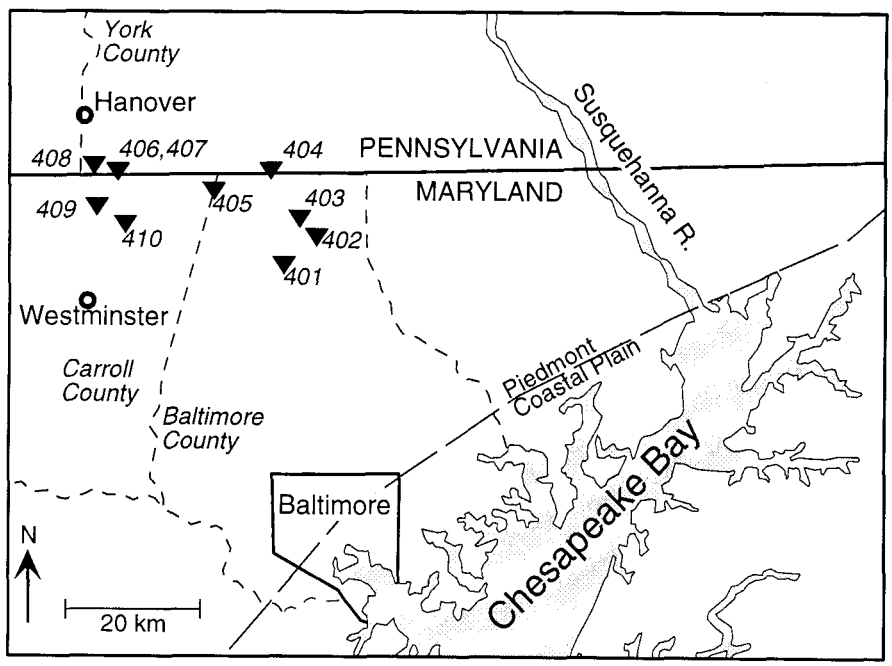

Figure 1. Locations of the Numbered Study Watersheds. The closely spaced watersheds 406 and 407 are represented by only one symbol.

float suspended in a stilling well connected to the stream. In the stream draining watershed 407, the depth was controlled by a 15.24 cm (6 in.) wide Parshall flume (Chow, 1964) immediately downstream. Water flow from watershed 407 was calculated by the known relationship between depth and flow in such a flume. Water flow from the other watersheds was calculated from rating curves of flow versus depth.

TABLE 1. Areas and Percentages of Land Use for Study Watersheds.

Watershed	Area (ha)	Percent Cropland	Percent Forest	Percent Other
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

Flow rates for rating curves were calculated from measurements of current velocity and depth made with a Price current meter on a wading rod at several locations along transects across the stream channels (Chow, 1964). For each stream, 10-19 measurements of flow rate were made during a range of high and low flow conditions throughout the study. Characteristics of the stream channels were mostly favorable for accurate rating curves. All the channels were clearly defined and incised 0.5-1 m. In four of the streams (401, 403, 405, and 409), small boulders (< 0.5 m) and cobbles produced turbulence and provided spaces for underflow, thus reducing the accuracy of our flow measurements. However, the other five streams had stable coarse-sand beds favoring accurate flow measurements.

The automated samplers used Campbell CR10 data loggers to record depth, calculate flow rate, and control pumps to take samples of stream water after a set amount of flow had occurred. Samples were pumped more frequently at higher flow rates, up to once every five minutes 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 was representative of discharge from overland storm-flow and from ground water emerging in the stream.

The sampling reported here covered a one year period from December, 1990 through November, 1991. During some weeks, the sampler failed or flow was too low to trigger an automatic sampling. Failures of the samplers were most commonly due to water freezing in the sampling hose in winter. About two-thirds of the weekly samples, on the average, were volume-weighted composites collected by the automated samplers. If a sample was not taken automatically, then a grab sample was taken in its place. Usually the weeks without automated sampling were weeks with persistent low flow, when automated sampling was not very important.

Besides using grab samples to replace missing composite samples, we took additional grab samples to characterize the partitioning of dissolved and particulate materials. We did not add preservative to these grab samples because the acid preservative dissolves some of the particulate nutrients. Instead, the samples were kept on ice and portions were filtered through a 0.45 μm membrane filter for separate analysis of dissolved nutrients. The unfiltered portions were then preserved with sulfuric acid and analyzed for particulate plus dissolved nutrients. Five such grab samples were taken from each stream at different stages of flow (including high flow) throughout the year. We also collected a grab sample every week for analysis of pH and alkalinity.

Chemical Analyses

We used the following techniques for analysis of N, P, and organic C species in the acid-preserved samples: total P was digested to phosphate (PO_4) with perchloric acid (King, 1932). PO_4 in the digestate and in undigested aliquots was analyzed by reaction with stannous chloride and ammonium molybdate (APHA, 1989). PO_4 in the undigested, acid-preserved samples is the total of dissolved and acid-extractable particulate phosphate. Total organic P (TOP) was calculated by subtracting total PO_4 from total P. Total Kjeldahl N was digested to ammonium (NH_4) with sulfuric acid, Hengar granules, and hydrogen peroxide (Martin, 1972). The NH_4 in the digestate was distilled and analyzed by Nesslerization (APHA, 1989). NH_4 in undigested aliquots was analyzed by oxidation to nitrite with alkaline hypochlorite (Strickland and Parsons, 1972) and analysis of the nitrite by reaction with sulfanilamide (APHA, 1989). NH_4 in the acid-preserved samples is the total of dissolved and acid-extractable particulate NH_4. Total organic N (TON)

was calculated by subtracting total NH_4 from total Kjeldahl N. The sum of nitrate and nitrite concentrations (NO_3) was measured by reducing nitrate to nitrite with cadmium amalgam, and analyzing nitrite by reaction with sulfanilamide (APHA, 1989). Total organic carbon (TOC) was analyzed by drying samples at 60°C, followed by reaction with potassium dichromate in 67 percent sulfuric acid at 100°C for three hours (Maciolek, 1962). Organic carbon was calculated from the amount of unreacted dichromate measured colorimetrically (Maciolek, 1962; Gaudy and Ramanathan, 1964).

We measured concentrations of suspended particles and dissolved silicate in the unpreserved composite samples. Particulate matter was analyzed by filtering a measured volume of the samples through a preweighed 0.45 μm membrane filter, rinsing with distilled water to remove salts, and then reweighing the filter after drying it in a vacuum desiccator. Dissolved silicate was analyzed in 0.45 μm filtered samples with a Technicon Auto-Analyzer II (method 696-82W).

We measured pH and alkalinity weekly in unpreserved grab samples. pH was measured in the laboratory with a Ross electrode after the sample equilibrated with air. Alkalinity was measured by titration as $CaCO_3$ equivalents (APHA, 1989).

RESULTS

Water Discharge

Discharge of water varied with rainfall and season. Heavy rainfall caused brief episodes of high discharge, but these generally accounted for a smaller fraction of the total flow than did base flow (e. g., Figure 2). The base flow rate varied with the frequency of high flow events and with seasonal changes in evapotranspiration. The highest base flows occurred in late winter and early spring (e. g., Figure 2). The total annual discharge of water per area differed greatly among the watersheds, ranging from 21-50 cm/yr (1 cm = 100 m^3/ha), or 23-55 percent of the precipitation input (Table 2). The differences in annual water efflux were not related to land use or size of the watershed. This suggests that some of the variation may be due to errors in our measurements of water flow.

TABLE 2. Annual Water Discharge (1 cm=100 m^3/ha) and Percent Yield of Precipitation Inputs for Study Watersheds. Precipitation during the study averaged 91.0 cm at three nearby weather stations of the Maryland State Climatologist (Millers 4 NE, 90.7 cm; Westminster Police Barracks, 91.2 cm; and Pretty Boy Reservoir, 91.2 cm). The long-term average precipitation at these stations was 113 cm/yr.

Watershed	Area (ha)	Discharge (cm/yr)	Percent Yield
401	117	50	55
402	596	48	53
403	3220	38	42
404	350	34	37
405	611	21	23
406	552	29	31
407	53.3	28	30
408	799	30	33
409	376	29	32
410	820	33	36
Average		**34**	**37**

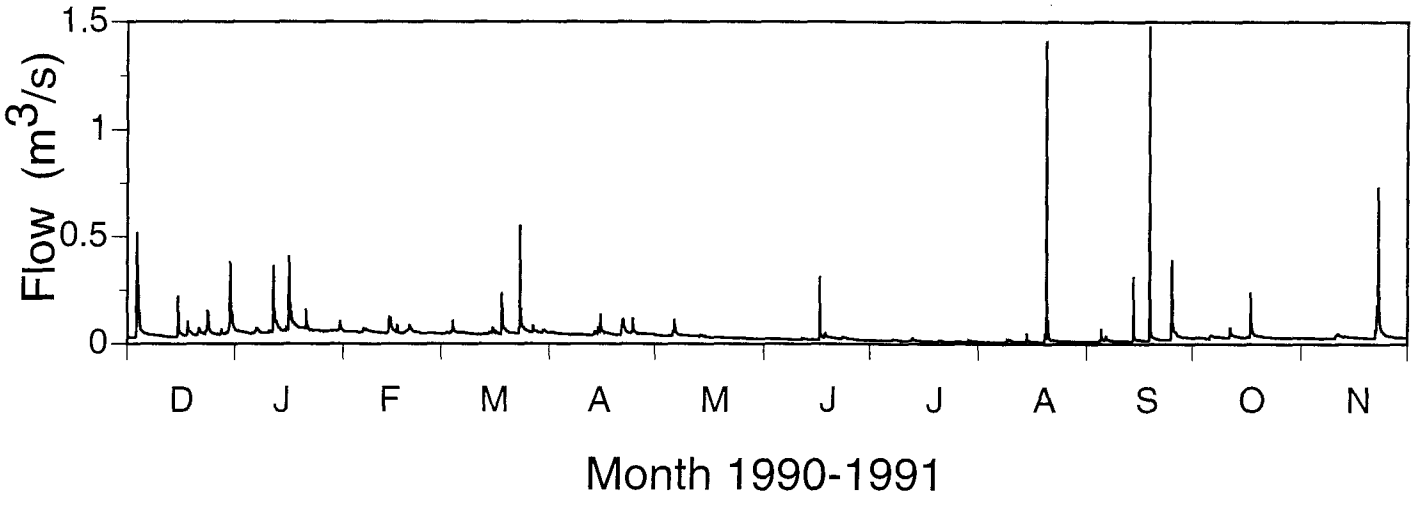

Figure 1. Annual Record of Stream Flow (m^3s^{-1}) at Watershed 405 for the Year of This Study.

Differences in measured water discharge lead to differences in calculated nutrient discharge. Therefore, to separate patterns in water quality from patterns of water discharge, we compared annual flow-weighted mean concentrations of nutrients calculated from the weekly flow and concentration data.

Material Concentrations

Annual flow-weighted mean concentrations of NO_3 and total N, which was 73-91 percent NO_3 (Table 3), increased dramatically as the proportion of cropland in the watershed increased (Figure 3). Adding a second land-use type as a regressor after percent cropland did not significantly improve the regressions for total N or NO_3 versus land use. TON and NH_4, which were minor components of total N, did not correlate significantly with land use (Figure 3). Dissolved Si declined slightly as cropland increased (Figure 4).

TABLE 3. Percentages of NO_3 in TN and the Atomic Ratios of TN:TP and Total Inorganic N to Total Inorganic P (TIN:TIP) in Discharges from the Different Watersheds.

Watershed	Percent NO_3	TN:TP	TIN:TIP
401	73	28	86
402	89	79	200
403	93	200	480
404	91	130	290
405	90	94	240
406	81	51	180
407	90	94	330
408	89	85	430
409	86	85	240
410	74	36	72

Unlike NO_3 and total N concentrations, P concentrations did not correlate significantly with any land use. However, the annual mean concentration of TOP increased significantly with the concentration of particulate matter (Figure 5), reflecting the predominance of particulate forms of TOP (Table 4). In grab samples taken over a range of stream stages, the median percentage of dissolved organic P in TOP was only 28 percent (Table 4). In contrast, TON, and TOC were predominately dissolved (Table 4). Although TOC was mostly dissolved, TOC concentration increased with the concentration of particulate matter (Figure 6).

Although concentrations of P species and total particulate matter did not correlate with land use, they differed significantly among watersheds ($p < 0.05$, ANOVA). Concentrations of P species were especially high in discharges from watershed 410, although these discharges did not contain proportionally high concentrations of suspended particles (Figure 6). Discharges from watershed 410 also had unusually high concentrations of TON, NH_4 (Figure 3), TOC (Figure 6), and alkalinity (Table 5). It is not clear why watershed 410 was so unusual or which nutrient fractions (dissolved or particulate) were unusually enriched.

The annual mean pH for watershed discharges ranged from 6.92-7.54 (Table 5). Discharges from the mostly-forested watershed 401 had the lowest mean pH and alkalinity (Table 5).

Since different factors influence N and P concentrations, the ratio of N:P concentrations in stream water differed widely among the watersheds but was not clearly correlated with any land use (Table 3). Atomic ratios of total N:total P ranged from 28-200, and ratios of inorganic N to inorganic P were even higher (72-480).

DISCUSSION

Water Discharge

Rates of water discharge from our watersheds (Table 2) were similar to or less than long-term mean rates for watersheds in the region of our study (Darling, 1962; Table 6). Discharge during our study may have been lower than the long-term mean because precipitation during our study (91 cm) was below the long-term average (113 cm). The long-term mean discharge rate for watersheds in our region was generally 41 cm/yr (Table 6), which is 37 percent of the long-term mean precipitation. Similarly, our study watersheds discharged an average of 36 percent of the precipitation during the study (Table 2).

Some of the variability in our measured rates of water discharge per area may arise from uncertainties of the true collection areas of the watersheds. We assume that the boundaries of our study watersheds coincide with the topographically-defined catchment of surface runoff. However, groundwater flow can cross these boundaries, so the true collection areas of streams may be larger or smaller than that implied by the surface topography. The uncertainty of the collection area should increase as the area of the watershed decreases because of the increase in the ratio of edge to area. Therefore, we would expect greater variability of water yields for smaller watersheds.

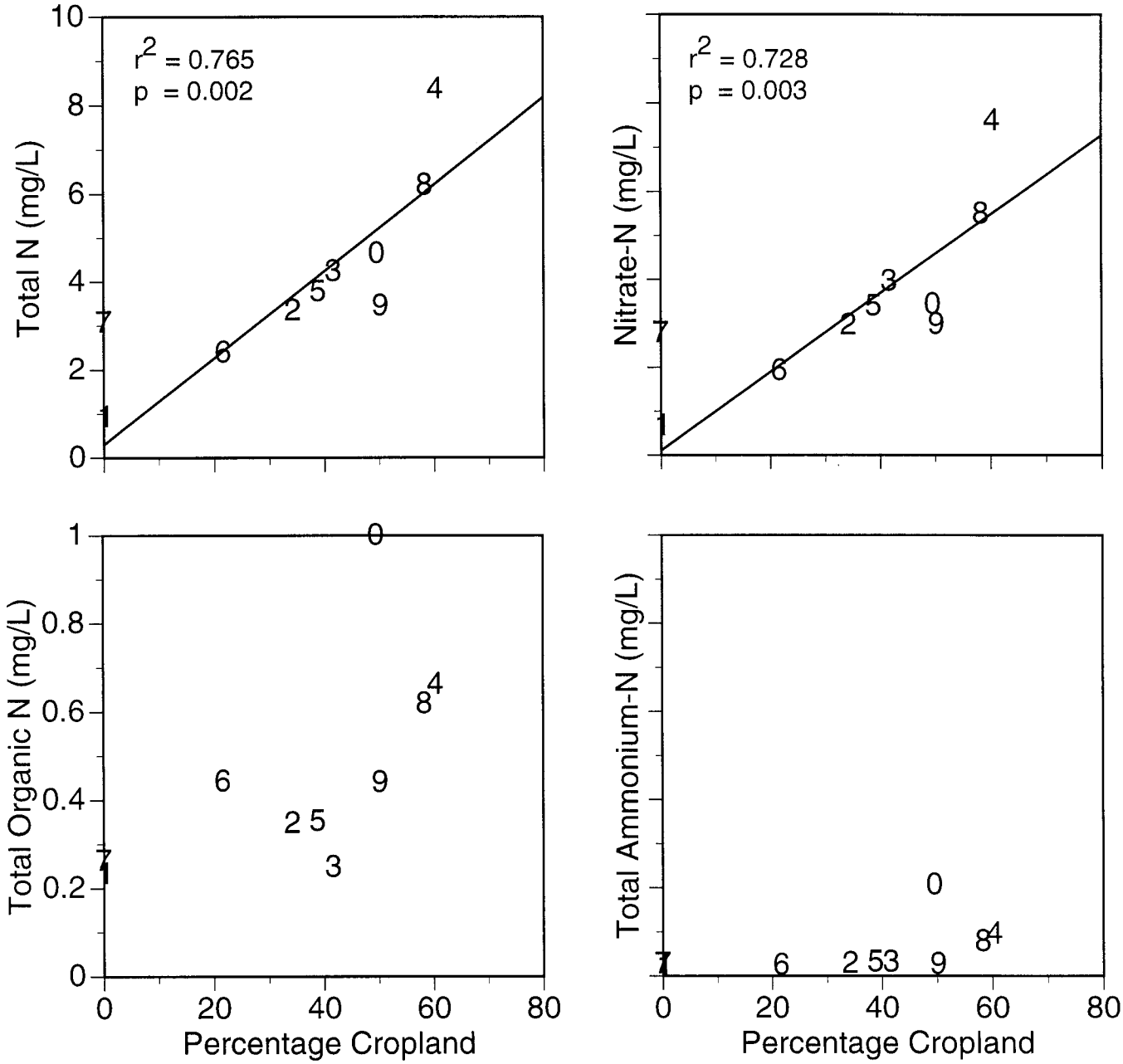

Figure 3. Flow-Weighted Mean Concentrations (mg N/L) of Total N, NO_3, TON, and NH_4 Versus the Percentage of Cropland in the Watersheds. Means are for one year of weekly integrated samples. Numbers representing data points refer to the watershed (1 = 401, 2 = 402, etc.). Lines fit by linear regression are shown when significant ($p < 0.05$).

Compared to our measurements, the discharge rates reviewed by Darling (1962) are probably more representative of typical rates for the region of the Piedmont we studied, because they are for larger watersheds and are averaged over a longer time period.

N and P Discharges

Several other studies have found that discharges of N and often P increase as the proportion of agricultural land increases (Hill, 1978; Neill, 1989; Mason *et al.*, 1990; Dillon and Kirchner, 1975; Rekolainen, 1990; Correll *et al.*, 1992; Nearing *et al.*, 1993), but some studies have found no apparent effect of agricultural land use on N and P discharges (Owens *et al.*,

1991; Thomas *et al.*, 1992). Since P discharge is related to transport of suspended particles, the influence of agriculture on P discharge may be outweighed by differences in the geochemistry and erodibility of sediments among watersheds (Grobler and Silberbauer, 1985; Vighi *et al.*, 1991; Dillon and Kirchner, 1975; Rekolainen, 1990).

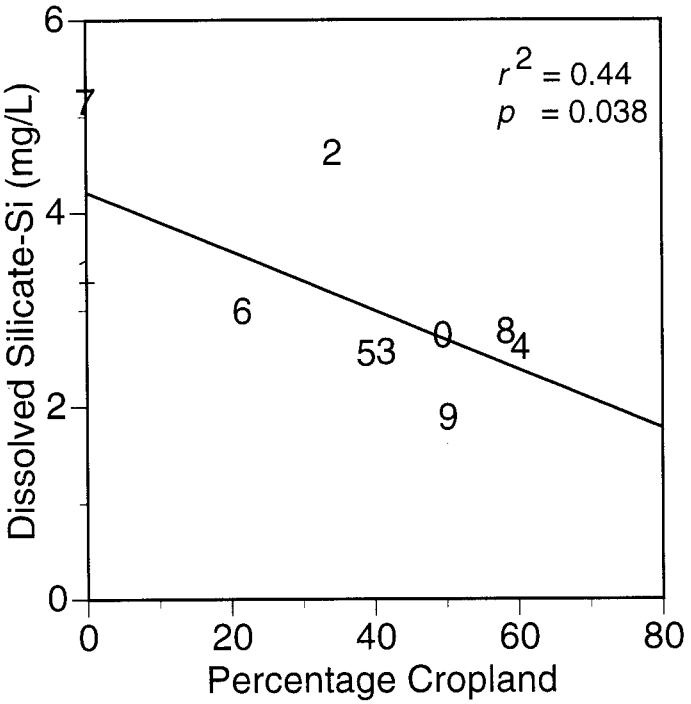

Figure 4. Flow-Weighted Mean Concentration of Dissolved Si (mg/L) Versus the Percentage of Cropland in the Watersheds. Means are for one year of weekly integrated samples. Numbers representing data points refer to the watershed (1 = 401, 2 = 402, etc.). The line was fit by linear regression.

Watershed discharges of P are often difficult to quantify because P is strongly associated with suspended particles which may be discharged primarily during short, unpredictable periods of high flow (Walling and Web, 1985; Kronvang, 1992). However, we were able to sample high flow episodes with our automated samplers. From our measurements of flow-weighted mean concentrations (Figure 5) and annual water discharge (Table 2), we estimated total P discharges ranging from 0.18-0.93 kg ha^{-1} yr^{-1} (Table 7).

Long-term average discharges of total P may be higher than those we measured because our study occurred during a relatively dry year. Assuming that total P concentrations are similar in an average year, we can estimate the total P discharge by multiplying concentration by the long-term regional mean rate of water discharge (Table 6). By this estimate, total P discharge ranges from 0.20-1.2 kg ha^{-1} yr^{-1} (Table 7).

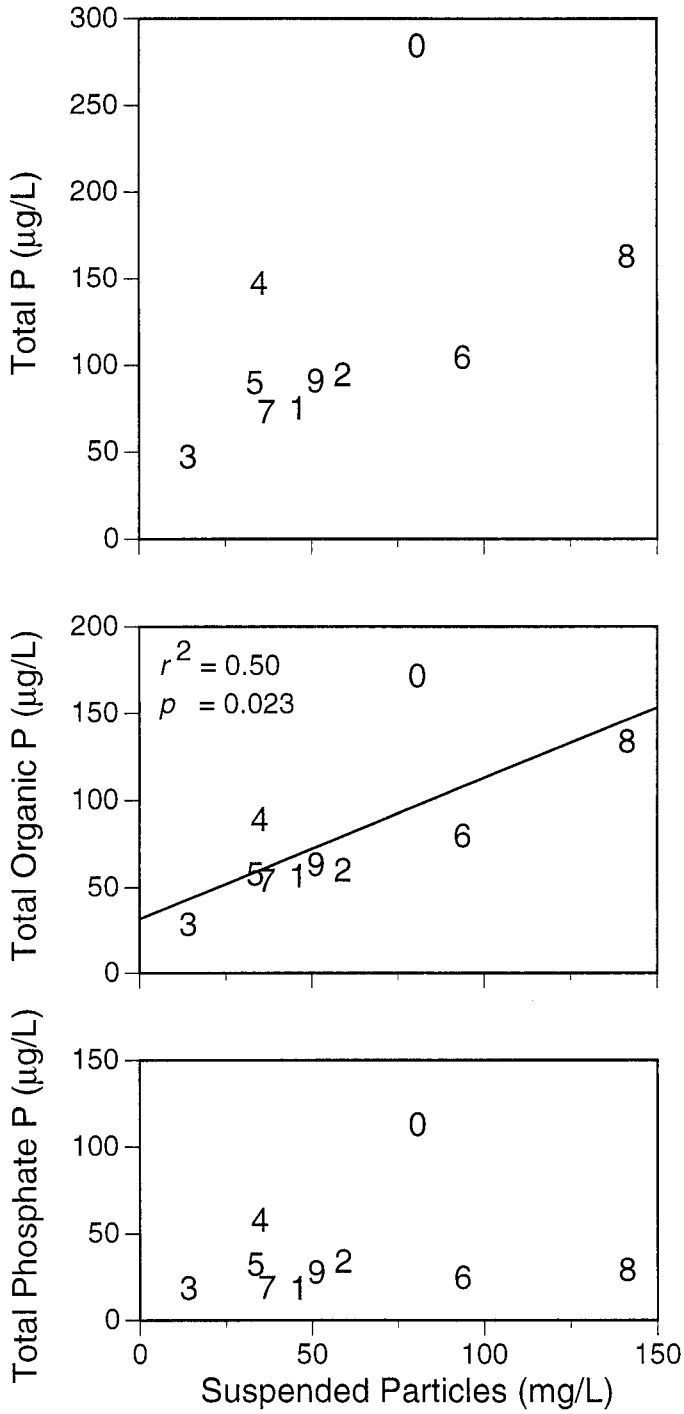

Figure 5. Flow-Weighted Mean Concentrations (µg P/L) of Total P, PO_4, and TOP Versus the Flow-Weighted Mean Concentrations of Suspended Particles (mg/L). Means are for one year of weekly integrated samples. Numbers representing data points refer to the watershed (1 = 401, 2 = 402, etc.). The line for TOP was fit by linear regression. Regressions for other data were not significant ($p > 0.05$).

TABLE 4. Median Percentages of Materials That Were Dissolved Rather Than Bound to Particles. These values were calculated by first finding the median value of five measurements for each watershed and then finding the median of the medians for all ten watersheds.

Species	Median Percent Dissolved	25th Percentile	75th Percentile
Phosphate	40	30	55
Organic P	28	2.7	76
Ammonium	50	28	83
Organic N	78	41	92
Organic C	74	58	86

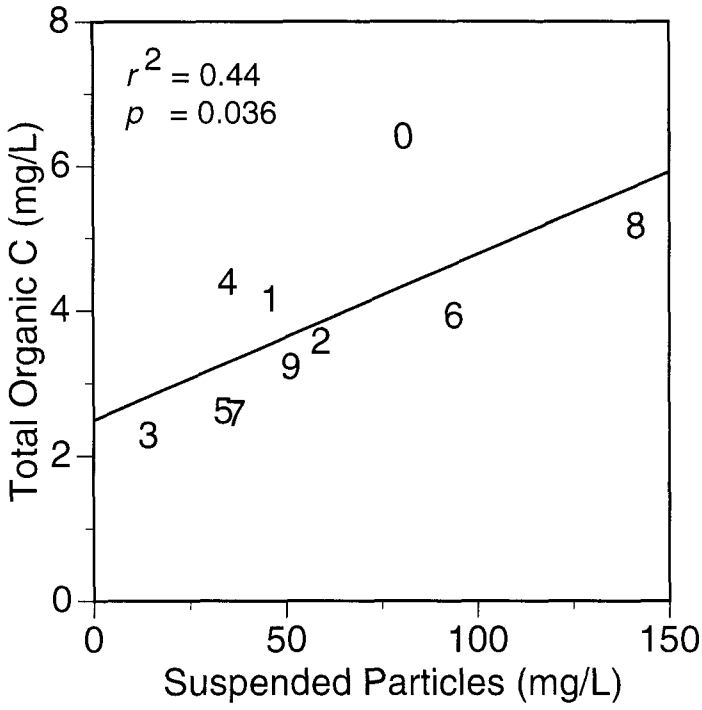

Figure 6. Flow-Weighted Mean Concentration of TOC (mg C/L) Versus the Flow-Weighted Mean Concentration of Suspended Particles (mg/L). Means are for one year of weekly integrated samples. Numbers representing data points refer to the watershed (1 = 401, 2 = 402, etc.). The line was fit by linear regression.

Our estimates of total P discharge fall within the range of others reviewed by Beaulac and Reckhow (1982) which averaged around 2 kg ha^{-1} yr^{-1} for row crops, 1 kg ha^{-1} yr^{-1} for pastures, and 0.2 kg ha^{-1} yr^{-1} for forests. For watersheds on the Coastal Plain of Chesapeake Bay, total P discharges varied with location but not land use, and covered a wider range, 0.07-4 kg ha^{-1} yr^{-1} (Jordan *et al.*, in press), than total P discharges of the Piedmont watersheds.

TABLE 5. Average Alkalinity (μeq/L) and pH in Weekly Grab Samples of Discharges from the Study Watersheds. For each watershed, data are averaged from about 50 samples taken during the one year study period.

Watershed	pH	Alkalinity (μeq/L)
401	6.92	153
402	7.00	314
403	7.23	295
404	6.94	471
405	7.17	363
406	7.26	416
407	7.12	335
408	7.23	475
409	7.48	473
410	7.54	890

TABLE 6. Data from Darling (1962) on Long-Term Average Annual Stream Discharges (cm/yr) and Drainage Areas (km^2) from the the Maryland Piedmont Near our Study Watersheds. Discharges were measured for 9-27-year periods ending in the 1950s.

Stream	Area (km^2)	Discharge (cm/yr)
Little Falls at Blue Mount	137	45
Slade Run at Glyndon	5.4	41
Western Run of Gunpowder River	155	41
Cranberry Branch and Westminster	8.5	41
North Branch at Cedarhurst	147	41

TABLE 7. Discharges of TP (kg ha^{-1} yr^{-1}) Calculated from Flow-Weighted Mean Concentrations and Two Different Estimates of Water Efflux: Our Own Measurements of Discharge During the One Year Study (Table 2) and the Long-Term Regional Mean Water Discharge Rate, 41.8 cm/yr (Table 6).

Watershed	Total P Discharge (kg ha^{-1} yr^{-1})	
	Measured Water Flow	Mean Water Flow
401	0.37	0.32
402	0.46	0.40
403	0.18	0.20
404	0.50	0.62
405	0.19	0.38
406	0.30	0.44
407	0.20	0.31
408	0.49	0.68
409	0.27	0.38
410	0.93	1.2

Most of the variability in the concentrations of total N and NO_3 was correlated with the proportion of cropland in our watersheds. However, NO_3 concentrations in discharges from the mostly-forested watershed 407 seemed anomalously high, averaging nearly 3 mg N /L (Figure 3). Comparing 153 streams in the Chesapeake Bay watershed, Correll and Weller (in press) found that NO_3 concentrations decreased as the proportion of forested land in the watershed increased, and that NO_3 concentrations were below 0.7 mg N/L in 13 streams with watersheds that were more than 85 percent forested. Similarly, a review by Stoddard (1994) reported median NO_3 concentrations of less than 0.9 mg N/L in streams with mostly-forested watersheds in the eastern United States. It is not clear why discharges from watershed 407 had such high NO_3 concentrations. Maybe watershed 407 receives influxes of NO_3-rich groundwater from nearby croplands that are outside the surface-water drainage boundary. The discrepancy between the surface-water drainage boundary and the true collection area of the watershed may be more significant for watershed 407 than for other watersheds we studied because watershed 407 was the smallest.

The discharge of N per ha of cropland or non-cropland can be estimated by extrapolation of a linear regression of the total N discharge rate against the percentage of cropland (Jordan *et al.* 1986). The results of this extrapolation depend on the data used in calculating N discharge (Figure 7). We can can either include watershed 407 in the regression or omit it as unrepresentative of mostly-forested watersheds. We can calculate N discharge from our measurements of water flow, or from the long-term regional mean rate of water flow (41.8 cm/yr, Table 6). If we use the long-term mean water discharge and omit the anomalously high discharge from watershed 407, we calculate that cropland discharges 42 kg N ha^{-1} yr^{-1} and non-cropland discharges 1.2 kg N ha^{-1} yr^{-1}. Including data from watershed 407 raises the predicted non-cropland discharge to 5.8 kg N ha^{-1} yr^{-1}, but the data for 407 seem very atypical for non-cropland, as previously discussed. Omitting 407 data, but using our measurements of water discharge instead of long-term means from Darling (1962) lowers the predicted cropland discharge to 32 kg N ha^{-1} yr^{-1}, partly because our study occurred in a dry year with less water discharge, and partly because the regression fit is not as tight (r^2 = 0.57 with our water flow measurements versus r^2 = 0.76 with the long-term mean). Using the long-term regional mean water discharge removes the variance introduced by differences in measured water flow among watersheds. Also, the long-term mean of water discharge may be better for predicting long-term mean N discharges than would our water flow measurements for a single dry year.

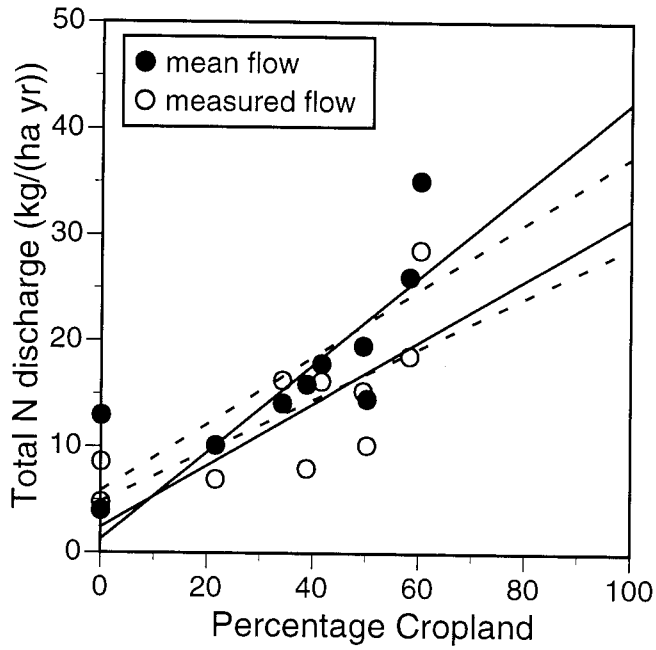

Figure 7. Total N Discharge (kg ha^{-1} yr^{-1}) Versus the Percentage of Cropland. Two values for N discharge are plotted: one (open circles) calculated by multiplying flow-weighted mean concentrations by our measurements of water flow and the other (closed circles) calculated by multiplying the concentrations by the long-term regional mean (Darling, 1962). Four significant ($p < 0.05$) regression lines are shown: solid lines are fit to data omitting the anomalously high discharge from watershed 407, dashed lines are fit to all data including 407. The steeper line of each pair is fit to the discharge values that were based on long-term mean flow, while the shallower is fit to the discharge values based on measured flows.

Our estimates for N discharge from non-cropland (1.2-5.8 kg N ha^{-1} yr^{-1} for 0 percent cropland, Figure 7) are similar to the medians reported by Beaulac and Reckhow (1982), 5 ha^{-1} yr^{-1} for pastures, and 2.5 kg ha^{-1} yr^{-1} for forests, and the rates used by Fisher and Oppenheimer (1991) to estimate N inputs to Chesapeake Bay, 5.8 kg N ha^{-1} yr^{-1} for pasture, and 1.4 kg N ha^{-1} yr^{-1} for forest. However, our estimates of N discharge from 100 percent cropland (29-42 kg N ha^{-1} yr^{-1}, Figure 7) are higher than the medians reported by Beaulac and Reckhow (1982), 9 kg ha^{-1} yr^{-1} for row crops and 15 kg ha^{-1} yr^{-1} for mixed agricultural land. The rates of N discharge we estimated for cropland in the Piedmont are much higher than estimates for cropland in the Coastal Plain (18 kg N ha^{-1} yr^{-1}, Jordan *et al.*, in press), or the rate assumed by Fisher and Oppenheimer (1991) in their calculation of N inputs to Chesapeake Bay (20 kg ha^{-1} yr^{-1}). Such large regional differences in the discharge of N suggest dramatic differences in N input, removal, storage, or transport processes in croplands of the Piedmont and Coastal Plain. These differences need

to be considered in estimating of N discharges from the Chesapeake Bay watershed.

Discharge rates estimated by extrapolating regressions should be interpreted cautiously. Discharge estimated by extrapolation may be much lower than the actual discharge at the edge of the crop field if adjacent non-croplands trap N released by the cropland (Peterjohn and Correll, 1984; Jordan *et al.*, 1986). The discharges from watersheds that we measured reflect interactions of different land use types within the watersheds. Also, it may be wrong to assume that if croplands were abandoned, the watershed discharges would eventually match the extrapolated estimates for non-cropland. Lands selected for crops had different characteristics historically than other lands, and these differences may affect N discharges even in absence of cultivation.

Effects of N Inputs

Our findings suggest that discharges of N, especially as NO_3 increase as anthropogenic inputs of N to croplands increase. For comparison to our discharge measurements, we estimated net anthropogenic inputs per area to croplands and non-croplands in the counties that included our study watersheds. Then we calculated the total net input to each study watershed by multiplying the areas of each land use type in each watershed by the estimated input rate per area for each land use type.

Anthropogenic N comes from many sources (Jordan and Weller, 1996). All lands in our watersheds receive NO_3 and NH_4 from atmospheric deposition, which has been greatly increased by human activities (Fisher and Oppenheimer, 1991). Agricultural lands also receive N from applications of fertilizer and from N-fixing crop plants. We consider N fixation by crop plants an anthropogenic input because it is fostered by human activity. N is removed from agricultural lands by the harvest of crops and by grazing. However, some of the N removed by grazing is reintroduced in livestock waste excreted on pastures. Livestock waste N that is not deposited on pastures may be applied to croplands. We account for all these inputs and outputs in our calculation of net anthropogenic N inputs.

Data for our calculation of anthropogenic N exchanges came from several sources. We used county-level estimates of wet atmospheric deposition compiled by the U. S. Geological Survey (Puckett, 1994; and personal communication) from data from the National Atmospheric Deposition Program (NADP, 1992). The total of wet and dry deposition was estimated by multiplying wet deposition by two (Fisher and Oppenheimer, 1991). Data on fertilizer applications for counties were obtained from Alexander and Smith (1990). We assume for simplicity that fertilizer is applied only to croplands. Data on crop harvests came from the 1987 census of agriculture (Bureau of the Census, 1993), and were converted to units of N as described by Jordan and Weller (1996). N fixation by crop plants was estimated from the areas of different crops (Bureau of the Census, 1993) and typical rates of N fixation (Jordan and Weller, 1996).

We calculated grazing and production of livestock waste from data on populations and diets of livestock. Grazed N was estimated for each county from the dietary demands of the grazing livestock and from the harvests of hay and silage crops that can substitute for grazed feed (Bureau of the Census, 1993; Jordan and Weller, 1996). Waste N deposited on pastures by grazers was estimated from the proportion of the diet grazed and the efficiency of incorporating N into livestock products (Jordan and Weller, 1996). N in livestock waste that was available for application to croplands was estimated by subtracting the waste N deposited on pastures from the total production of waste N calculated from livestock populations in the counties (Bureau of the Census, 1993) and livestock production efficiencies (Jordan and Weller, 1996).

We assume that most of the livestock waste available for application to croplands is applied evenly to the croplands in the same county where the waste is produced. However, much N can be lost from livestock waste by volatilization of NH3 before and after application to croplands. Typically, 10-40 percent of the N in livestock waste can be released as NH_3 gas (ApSimon *et al.*, 1987; Schlesinger and Hartley, 1992). Poultry waste can lose more than half its N as NH_3, depending on handling and storage (Giddens and Rao, 1975; Sims and Wolf, 1994). Because of these potential losses, the amount of N introduced to croplands as livestock waste is probably the most uncertain quantity in our estimate of net anthropogenic N inputs. Therefore, we estimated ranges of net anthropogenic N inputs to croplands assuming no loss and 50 percent loss of N from livestock waste.

There were some differences in anthropogenic N inputs among the three counties that contained our study watersheds (Table 8). However, we averaged the input rates for the three counties to estimate the rates for our study watersheds because the watersheds are all located near the junction of the counties. In two of the three counties, fertilizer was the main source of anthropogenic N for croplands, but in York county, where livestock waste production was highest and fertilizer application was lowest, livestock waste may have exceeded fertilizer as an N source to

cropland. This probably reflects a substitution of manure for chemical fertilizer in areas where manure is abundant. Harvest removed about half of the N input to croplands, leaving an average net input of 97-71 kg N ha^{-1} yr^{-1}. We assumed that N inputs to pastures from N fixation and livestock waste are counter-balanced by removals due to grazing (Jordan *et al.*, in press), so that net anthropogenic input to pasture lands, forests, and other non-croplands equals wet plus dry atmospheric deposition, 14 kg ha^{-1} yr^{-1}.

We calculated the net anthropogenic input of N to each study watershed using data on land use (Table 1) and rates of input for croplands (71-97 kg ha^{-1} yr^{-1}) and non-croplands (14 kg ha^{-1} yr^{-1}). Estimates of anthropogenic inputs differ according to whether or not we assume loss of livestock waste N by NH_3 volatilization. Estimates of N discharges also differ according to whether we calculate N discharge based on our measurements of water flow or based on the long-term regional mean water flow rate (Table 9). However, regardless of the set of assumptions we choose, it is clear that the watershed discharge of N usually represents less than half of the net anthropogenic input. One notable exception is the mostly-forested watershed 407 which discharged 61 percent or 93 percent of the anthropogenic input, depending on whether we calculate N discharge from our measurements of water efflux or from the long-term regional mean rate. However, as previously discussed, NO_3 concentrations in discharges from this watershed were anomalously high possibly due to anthropogenic inputs from outside the surface drainage boundaries of the watershed. In general, most of the anthropogenic N input is apparently not discharged in streams. The anthropogenic N that is not discharged must be either stored in groundwater, soil organic matter, or biomass, or converted to gaseous forms and released to the atmosphere.

TABLE 9. Net Anthropogenic Inputs of N to Watersheds Compared to Discharges of N. Anthropogenic inputs are calculated by multiplying average rates of input for croplands (71-97 kg N ha^{-1} yr^{-1}, Table 8) and other lands (14 kg N ha^{-1} yr^{-1}) by the areas of these land types in each watershed (Table 1). The range of input values results from the alternative assumptions of either 50 percent or 0 percent loss of N from livestock waste before application to croplands. Two values for N discharge are shown: one calculated by multiplying flow weighted mean concentrations by our measurements of water flow and the other calculated by multiplying the concentrations by the long-term regional mean flow based on data from Darling (1962).

Watershed	Net Anthropogenic N (kg ha^{-1} yr^{-1})	Total N Discharge (kg ha^{-1} yr^{-1})	
		Measured Flow	Mean Flow
401	14-14	4.8	4.0
402	33-42	16	14
403	38-49	16	18
404	48-64	29	35
405	36-46	8.0	16
406	26-32	6.9	10
407	14-14	8.6	13
408	47-62	19	26
409	43-56	10	15
410	42-55	15	20

Riverine discharges account for less than one third of anthropogenic N inputs even for whole river basins, such as the Mississippi drainage (Jordan and Weller, 1996; Howarth *et al.*, 1996). Anthropogenic N may accumulate as organic nitrogen in forest soil and wood. Forests in the United States, especially in the Northeast, are accumulating organic matter in part due to the abundance of young stands on land recently abandoned from agriculture (Turner *et al.*, 1995). Forest growth throughout the world may also be enhanced by increases in atmospheric carbon dioxide

TABLE 8. Net Anthropogenic Inputs of N to Cropland (kg ha^{-1} yr^{-1}) in Counties Containing the Study Watersheds. Atmospheric deposition in wet and dryfall was estimated as two times wetfall. Livestock waste includes only waste that is not deposited on pastures. The range of values for livestock waste reflects either assuming 50 percent of the N is lost in transfer to croplands or none is lost. N fixation is for crop plants. Net Input is the sum of all the inputs minus the N removed by harvests of crops.

County	Atmospheric Deposition	Fertilizer	Livestock Waste	N Fixation by Crops	Harvest	Net Input
Baltimore, Maryland	13	94	22-43	36	89	76-97
Carroll, Maryland	14	88	29-57	37	77	91-119
York, Pennsylvania	15	39	30-60	32	71	45-75
Average	**14**	**74**	**27-53**	**35**	**79**	**71-97**

and deposition of nitrogen (Schindler and Bayley, 1993). Some anthropogenic nitrogen may also accumulate in groundwater. Many studies show increasing trends in the NO_3 concentration of ground water (Power and Schepers, 1989; Strebel *et al.*, 1989), but it is not known how much nitrogen is accumulating there or how fast ground water nitrogen is released to surface waters. Much of the anthropogenic nitrogen may eventually be converted to dinitrogen, nitrous oxide, or nitric oxide gases through denitrification. Nitric oxide contributes to acid deposition (Cicerone, 1989) while nitrous oxide contributes to global warming (Abrahamson, 1989; Lal and Holt, 1991), and depletion of stratospheric ozone (Bolin *et al.*, 1983). Global increases in atmospheric nitrous oxide (Rasmussen and Khalil, 1986; Pearman *et al.*, 1986) suggest that global increases in denitrification may parallel global increases in anthropogenic nitrogen inputs.

Comparison to Coastal Plain Watersheds

The Coastal Plain watersheds that we have studied release an even smaller proportion of the anthropogenic N input (usually < 30 percent; Jordan *et al.*, in press) than do the Piedmont watersheds, although croplands in the Coastal Plain receive similar anthropogenic inputs to those of the Piedmont. This suggests that the Coastal Plain watersheds are more effective at storing N or converting N to gaseous forms. On the Coastal Plain, agricultural fields are typically located on well drained uplands above poorly drained riparian forests (Gilliam and Skaggs, 1988; Correll, 1991), which can retain 70-90 percent of the total N inputs which enter mainly as NO_3 in subsurface discharges from adjacent cropland (Lowrance *et al.*, 1984; Peterjohn and Correll, 1984; Jacobs and Gilliam, 1985; Lowrance *et al.*, 1985; Peterjohn and Correll, 1986; Jordan *et al.*, 1993). It is hypothesized that a major fate of the N retained by riparian forests is conversion to gaseous N by denitrification (Lowrance *et al.*, 1984; Peterjohn and Correll, 1984; Jacobs and Gilliam, 1985; Haycock and Pinay, 1993), but much of the evidence for this is circumstantial (Lowrance, 1992; Weller *et al.*, 1994). Environmental conditions are often favorable for denitrification and high potentials for denitrification have been measured (Peterjohn and Correll, 1984; Jacobs and Gilliam, 1985; Lowrance and Pionke, 1989; Groffman *et al.*, 1991; Schipper *et al.*, 1993; Fustec *et al.*, 1991; Pinay and Decamps, 1988). However, direct measurements of denitrification are limited by the lack of accurate field methods (Sprent, 1987; Tiedje *et al.*, 1989) and by the enormous spatial and temporal variability of denitrification rates (Folorunso and Rolston, 1984; Weller et al., 1994).

It is not known whether riparian forests in the Piedmont can intercept N as effectively as those in the Coastal Plain (Lowrance *et al.*, 1995). Ground water flow patterns in the Piedmont may not be as favorable as in the Coastal Plain for N uptake in riparian zones. In the Coastal Plain, layers of impermeable sediment can force ground water flow near the soil surface in riparian zones and thereby enhance the potential for denitrification and N uptake by plants (Jordan *et al.*, 1993). In the Piedmont, ground water 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 N 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.

The N, P, dissolved Si, and TOC discharged by watersheds contribute to eutrophication of receiving waters. Concentrations of dissolved Si (Figure 4) and TOC (Figure 6) were not as variable as concentrations of N (Figure 3) and P (Figure 5). N and P were discharged in widely different proportions by different types of watersheds, but the atomic ratios of N:P discharged were always much higher than 16 (Table 3), 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 ratios of N:P have also been found in discharges from major tributaries to Chesapeake Bay, the Potomac River (N:P = 23, Jaworski *et al.*, 1992) and the Susquehanna River (N:P = 66; Ott *et al.*, 1991). In contrast, discharges from some of the Coastal Plain watersheds we have studied have N:P ratios less than 16 (Jordan *et al.*, in press), which would favor N limitation. Also, the dissolved Si concentrations in discharges from the Coastal Plain were generally higher (3-10 mg/L; Jordan *et al.*, in press) than in discharges from the Piedmont (2-5 mg/L, Figure 4), suggesting that Coastal Plain discharges would support more diatom growth than would Piedmont discharges.

The most dramatic difference between Piedmont and Coastal Plain watersheds is in the effect of cropland on N discharge. Croplands of the Piedmont seem to discharge more than twice as much N per ha than those of the Coastal Plain. This difference is not due to a difference in the amount anthropogenic N input to the watersheds. Estimated inputs to croplands in the Piedmont counties ranged from 45-91 kg N ha^{-1} yr^{-1}, assuming 50 percent loss of N from livestock waste (Table 8), and inputs to Coastal Plain counties,

estimated by the same method, ranged from 66-160 kg N ha^{-1} yr^{-1} (Jordan *et al.*, in press). Clearly, the effects of land use on nutrient input to Chesapeake Bay can not be evaluated without considering the effects of the physiographic region. More research is needed to elucidate the underlying mechanisms that account for the differences in N processing by Piedmont and Coastal Plain watersheds.

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