Effects of Agriculture on Discharges of Nutrients from Coastal Plain Watersheds of Chesapeake Bay

Thomas E. Jordan,* David L. Correll, and Donald E. Weller

ABSTRACT

We measured annual discharges of water, sediments, and nutrients from 17 Chesapeake Bay watersheds with differing proportions of agricultural lands on the inner, central, and outer Coastal Plain. In all regions of the Coastal Plain, the flow-weighted mean concentrations of N species in watershed discharge increased as the proportion of cropland in the watershed increased. In contrast, the concentrations of P species did not correlate with any land use. Instead, P concentrations correlated with the concentration of suspended particles, which differed greatly among watersheds in different regions of the Coastal Plain. Consequently, the ratio of N/P in discharges differed widely among watersheds, potentially affecting N or P limitation of phytoplankton growth in the receiving waters. Concentrations of dissolved silicate, organic C, pH, and alkalinity in discharges did not differ greatly among watersheds or correlate with land use. Nitrogen discharge correlated with net anthropogenic inputs of N to the watershed, but usually less than one-third of the net anthropogenic inputs were discharged.

AGRICULTURAL activities can increase fluvial discharges of nutrients, but the magnitude of the effect of agriculture is difficult to predict. Watersheds with greater proportions of agricultural land have been found to discharge greater amounts of N (Hill, 1978; Neill, 1989; Mason et al., 1990), P (Dillon and Kirchner, 1975), or both nutrients (Rekolainen, 1990; Correll et al., 1992; Nearing et al., 1993). Such observations have led to the derivation of nutrient export coefficients for particular land use types, such as croplands, pastures, and forests (Beaulac and Reckhow, 1982). However, uniform export coefficients may be poor predictors of nutrient discharges because export rates for given land types can differ widely (Frink, 1991). Some studies of small watersheds have found no correlation at all between the proportion of agricultural land and discharges of N and P by streams (Thomas et al., 1992). For larger drainage basins (0.2–1.3 × 106 km^2), nitrate discharge is poorly correlated with the proportion of cropland, but highly correlated with anthropogenic input of N from atmospheric deposition, fertilizer application, cultivation of N_2-fixing crops, and net import of agricultural products (Jordan and Weller, 1996). In contrast, discharges of P may be more strongly influenced by geologic factors than by anthropogenic inputs. For example, discharges of P from some watersheds were found to be related to rates of erosion but not to rates of application of P fertilizer (Vighi et al., 1991). Also, watersheds with igneous rock substrates have been found to discharge less P than watersheds with sedimentary rocks (Dillon and Kirchner, 1975; Grobler and Silberbauer, 1985).

Despite uncertainties in measuring and predicting the effects of agriculture, it is clear that agriculture has played an important role in the recent increases in nutrient delivery to coastal waters and the consequent acceleration of eutrophication (Nixon, 1995). For example, increases in fertilizer applications have been linked to increases in nutrient discharges by the Mississippi River (Turner and Rabalais, 1991). Agriculture is also a major source of nutrient discharge from the watershed of Chesapeake Bay (Fisher and Oppenheimer, 1991; Jaworski et al., 1992; Vaithiyanathan and Correll, 1992). Watershed inputs of both N and P 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) that 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). Excessive N and P inputs have also led to seasonal depletion of dissolved silicate resulting in altered phytoplankton production and species composition in the middle to lower Chesapeake Bay (D'Elia et al., 1983; Anderson, 1986; Conley and Malone, 1992).

The Chesapeake Bay watershed includes land in three physiographic provinces: the Coastal Plain, the Piedmont, and the Appalachian. About 17% of the 178 000 km^2 watershed of Chesapeake Bay and all of the land adjacent to the shoreline is in the Coastal Plain (NCRI Chesapeake, 1982). The Coastal Plain includes about 24% of the agricultural land in the Chesapeake Bay watershed (NCRI Chesapeake, 1982). Along the eastern shore of the Chesapeake are areas where corn (*Zea mays* L.) and soybean [*Glycine max* (L.) Merr.] production match that of the central U.S. Corn Belt (Thomas and Gilliam, 1977). Further south on the Delmarva Peninsula, one of the largest concentrations of poultry farms in the U.S. produces a very serious problem of manure disposal (Sims and Wolf, 1994). The western shore of the Chesepeake is characterized by less intensive and less extensive agriculture than the eastern shore. The topography of the Coastal Plain varies from the rolling hills of the inner Coastal Plain on the western shore and 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.

This study investigates the effects of agricultural land use and nutrient loading on discharges of water, sediments, and nutrients from Coastal Plain watersheds of the Chesapeake Bay. We compare annual mean nutrient concentrations and discharges from 17 watersheds with differing proportions of agricultural lands in the inner, central, and outer coastal plain. We also calculate the

Smithsonian Environmental Research Center, Edgewater, MD 21037.
Received 23 Feb. 1996. *Corresponding author (jordan@serc.si.edu).

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Abbreviations: TOP, total organic P; TON, total organic N; TOC, total organic carbon.

net anthropogenic input of N to these watersheds and the proportion of the N input that was discharged.

METHODS

Study Watersheds

The study watersheds were distributed in four clusters throughout the Coastal Plain of the Chesapeake drainage (Fig. 1). The clusters were located in three different sections of the Coastal Plain (inner, central, and outer), defined by distance from the edge of the Piedmont. We have studied one cluster on the inner Coastal Plain for more than 20 yr (e.g., Correll, 1977; Jordan et al., 1986a; 1991a). It includes seven watersheds in the drainage of the Rhode River, a small subestuary on the western shore of the Chesapeake. Another cluster on the inner Coastal Plain was at the northern end of the Delmarva Peninsula. A cluster on the central Coastal Plain was in an area of high intensity corn and soybean farming, and a cluster on the outer Coastal Plain was in an area of intensive poultry farming.

The watersheds were mostly 100 to 2000 ha in area and were composed of 0 to 67% cropland and 0 to 56% managed grassland (Table 1). Areas of land use patches were measured from 1:2400 monochrome aerial photographs (provided by Anne Arundel County Planning Office, 1984) for the Rhode River sites, and from 1:9600 scale color-infrared aerial photographs (NAPP, 1991) for other watersheds. Classifications of land use were verified from land-based observations made during the study. The watersheds had low human populations and no sewage outfalls.

Flow Measurements and Sampling

We used automated samplers to monitor discharges of water, nutrients, and sediment from the streams that drain the

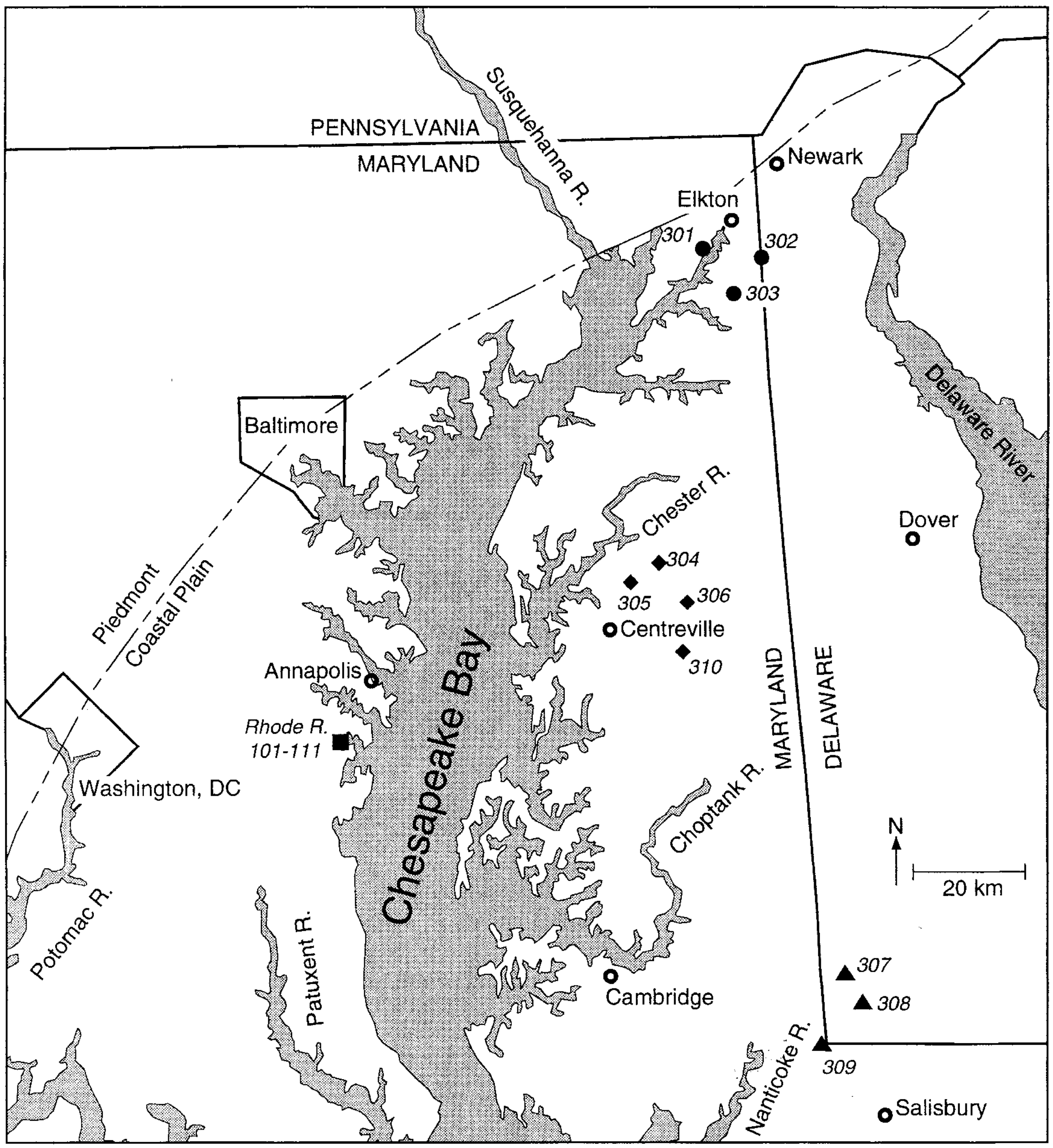

Fig. 1. Locations of the numbered study watersheds on the inner (101–303), central (304–306, 310), and outer (307–309) Coastal Plain. One symbol represents seven closely spaced watersheds of the Rhode River.

Table 1. Total areas (ha) and percentages of land use types for inner, central, and outer Coastal Plain watersheds. The two clusters of inner Coastal Plain watersheds include a cluster in the Rhode River watershed and a cluster on the Delmarva Peninsula. The category grassland includes pasture, hayfields, and other managed grasslands. Forest also includes oldfield and orchard. Pond also includes herbaceous wetland. "Resid&Rd" includes residential yards, farmyards, buildings, and roads.

Watershed	Area (ha)	Rowcrop	Grassland	Forest	Fallow	Pond	Resid&Rd
Inter Coastal Plain							
Rhode River							
101	226	2.3	21.9	52.4	10.	1.1	13.1
102	193	6.2	19.5	59.6	1.2	0.4	13.7
103	247	1.7	12.5	71.0	2.1	0.3	12.3
108	150	26.3	13.5	51.6	2.7	0.1	5.8
109	17.0	60.2	0	34.6	0	0	5.2
110	6.2	0	0	98.2	0	0	1.8
111	5.5	0	0	11.3	88.6	0	0
Delmarva							
301	569	0.3	0	98.3	0.7	0.4	0.3
302	971	28.1	3.3	50.6	10.2	0.1	8.7
303	478	15.0	56.2	25.3	1.4	0.1	2.1
Central Coastal Plain							
304	1077	66.3	0	30.4	1.1	0.1	1.9
305	1757	59.8	7.6	28.8	0.1	0.5	1.4
306	684	66.7	2.7	28.3	0	0.5	1.7
310	5240	67.0	1.0	27.0	2.2	0.3	2.3
Outer Coastal Plain							
307	139	1.3	0	88.8	9.9	0	0
308	1241	45.6	0	52.0	0.5	0	2.0
309	1632	41.3	0.6	56.9	0.1	0.2	0.9

study watersheds (Table 2). Automation ensures adequate sampling of particulate fractions in storm-flow (e.g., Jordan et al., 1986b). At the Rhode River site, the samplers employ V-notch weirs to measure flow (Correll, 1977, 1981). At the other watersheds the samplers monitored stream depth and calculated water flow from rating curves of flow vs. depth.

Flow rates for rating curves were calculated from measurements of current velocity and depth made at several locations across the stream channels using a Price current meter on a wading rod (Chow, 1964). For each stream, 11 to 35 measurements of flow rate were made during a range of high and low flow conditions throughout the study. Regressions of the logarithm of flow rate against the logarithm of depth had coefficients of determination (r^2) >0.79. For 7 of the 10 streams without V-notch weirs, a single regression was sufficient to define the rating curve, but at three of the streams more than one regression was needed because slopes differed for different depth ranges.

The automated samplers without weirs used Campbell CR10 data loggers to record depth, calculate flow, and control pumps to take samples of stream water after a set amount of flow had occurred. Samples were pumped through plastic tubing that was first rinsed with stream water. Samplers for the Rhode River watersheds were designed differently, but also pumped samples after a set amount of flow occurred (Correll, 1977, 1981). Thus, for all watersheds, samples were pumped more frequently at higher flow rates, up to once every 5 min during storm flow (e.g., Fig. 2). Two sets of flow-weighted composite samples, one with sulfuric acid as a preservative, were collected weekly for analysis.

The composition of the composite samples was representative of discharge from overland storm-flow and from groundwater emerging in the stream, but not representative of bedload. Sample inlets for streams with weirs were located at the bottom of the V-notch. Sample inlets for other streams were in the middle of the stream. All sample inlets were high enough above the bottom to avoid sampling bedload. We assume that the streams were small enough (1–5 m wide and <0.5 m deep at baseflow) to be well mixed throughout their cross-sections.

The sampling reported here covered a 1-yr period from December 1990 through November 1991. All the watersheds were studied concurrently. During some weeks, flow was either too low to generate an automatic sample, or the sampler failed. Failures of the samplers were most commonly due to water freezing in the sampling hose in winter. If a sample was

Table 2. Locations of automated samplers.

Watershed	Latitude N.	Longitude W.	Stream name	Tributary to	Road crossing
101	38°53′26.1″	76°33′28.0″	North Br.	Muddy Cr.	None
102	38°53′16.9″	76°33′51.8″	Blue Jay Br.	Muddy Cr.	Old Muddy Cr. Rd.
103	38°53′21.4″	76°34′08.3″	Williamson Br.	Muddy Cr.	MD468
108	38°52′26.0″	76°33′15.1″	Steinlein Br.	Muddy Cr.	None
109	38°52′09.0″	76°33′13.0″	None	Steinlein Br.	None
110	38°53′02.4″	76°33′13.1″	None	Muddy Cr.	None
111	38°53′37.3″	76°33′21.0″	None	Muddy Cr.	None
301	39°34′06.2″	75°53′08.9″	E. Fork, Plum Cr.	Elk R.	None
302	39°33′16.6″	75°46′52.7″	Long Branch Cr.	Elk R.	None
303	39°30′20.6″	75°49′57.7″	Herring Cr.	Elk R.	MD 213
304	39°07′57.4″	75°58′33.8″	N. Br., Southeast Cr.	Chester R.	MD 19
305	39°06′24.9″	76°01′38.5″	Granny Finley Br.	Chester R.	MD 213
306	39°04′39.5″	75°55′37.3″	Upper German Br.	Choptank R.	Murphy Rd.
310	39°00′32.2″	75°56′15.0″	German Br.	Choptank R.	MD 304
307	38°33′40.4″	75°39′48.7″	None	Naticoke R.	None
208	38°31′12.3″	75°38′01.7″	Tussocky Br.	Naticoke R.	MD 24
309	38°27′48.3″	75°42′28.0″	Mockingbird Cr.	Naticoke R.	MD 54

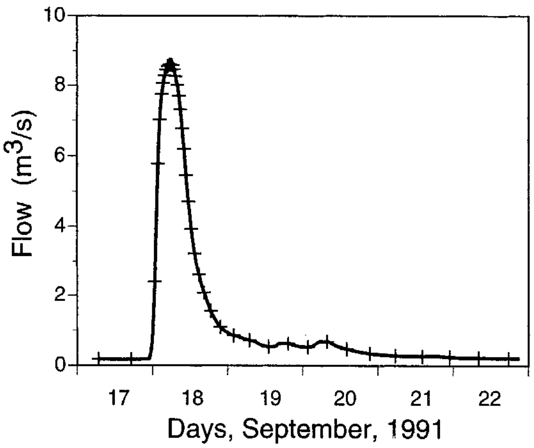

Fig. 2. A 6-d record of stream flow (m^3/s) from the automated sampler at watershed 310. Crosses indicate times when samples were pumped. The data logger regulated the pumping frequency to be proportional to the stream flow.

not taken automatically, then a grab sample was taken in its place. Usually such grab samples were needed only for weeks with persistent low flow, when automated sampling of high flow episodes was unnecessary. About two-thirds of the weekly samples, on the average, were volume-weighted composites collected automatically by the samplers, but one automated sampler (watershed 111) did not function at all during our study period. Weekly grab samples were substituted when persistent low flow, freezing water, or malfunctions prevented automated sampling.

Besides using grab samples to replace missing composite samples, we took additional grab samples to characterize the partitioning of dissolved and particulate materials. These grab samples were taken at different stages of flow (including high flow) throughout the year. We did not add preservatives 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. We also collected another grab sample every week for analysis of pH and alkalinity.

We compared water discharges to precipitation. Precipitation near the Rhode River sites was measured with a standard weather-bureau manual rain gauge (Jordan et al. 1995). Precipitation at other watersheds was estimated from monthly precipitation records from nearby weather stations reporting to the Maryland State Climatologist. Data from stations at Chestertown, Millington, the Conowingo Dam, and Newark University Farm were averaged for sites on the northern Delmarva Penninsula, data from Chestertown and Millington were averaged for the Central Coastal Plain, and data from Salisbury and Vienna were averaged for the Outer Coastal Plain.

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). Phosphate in the undigested, acid-preserved samples is the total of dissolved and acid-extractable particulate PO_4. The concentration of this total reactive PO_4 was subtracted from the concentration of total P to calculate the concentration of total organic P (TOP). 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). Ammonium 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). Ammonium 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% sulfuric acid at 100°C for 3 h (Maciolek, 1962). Organic C was calculated from the amount of unreacted dichromate measured colorimetrically (Maciolek, 1962; Gaudy and Ramanathan, 1964). Preliminary checks indicated that chloride concentrations were too low (<100 mg/L) to interfere with the TOC analysis (Dobbs and Williams, 1963). Studies of the acid preservation showed no detectable conversion of organic P, N, or C to inorganic forms due to the preservative.

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

Water discharge varied with rainfall and season. Typically, heavy rainfall caused brief episodes of high discharge that were an important fraction of the total discharge (e.g., Fig. 3). The baseflow between episodes of high flow varied with the frequency of high flow events and with seasonal changes in evapotranspiration. Baseflow from the Delmarva watersheds reached a minimum in June and July and then increased after a series of storms in late July and early August (e.g., Fig. 3). Flow from the Rhode River watersheds, other than 101 and 111, ceased entirely for several weeks during summer and late fall.

The total annual discharge of water per area differed greatly among the watersheds (Table 3), ranging from 11 to 48 cm/yr (1 cm = 100 m^3/ha). The differences in annual discharge could not be explained by differences in rainfall, which ranged from 95 to 106 cm (Table 3). The discharge rate was lower for smaller watersheds, except on the Inner Coastal Plain of the Delmarva peninsula. All of the watersheds discharging <25 cm were <700 ha in area (Table 3). Differences in water discharge influence the calculation of nutrient discharge. Therefore, to examine patterns in water quality inde-

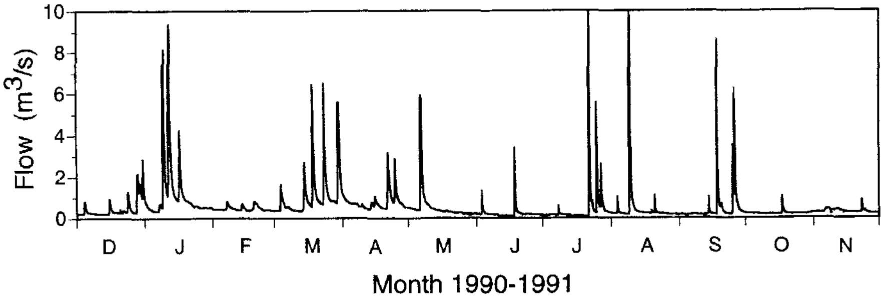

Fig. 3. Stream flow (m^3/s) at watershed 310 for the year of this study.

pendently 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 N species increased as the proportion of cropland in the watershed increased (Fig. 4). The correlation was much stronger for NO_3 and total N than for TON or total NH_4. Thus, the percent of total N composed of NO_3 increased as the proportion of cropland increased (Fig. 5). Total N was more than 60% NO_3 for all but one of the watersheds that were more than 30% cropland. For two outer Coastal Plain watersheds with more than 40% cropland, NO_3 concentrations were unusally high and TON concentrations were unusually low. For those watersheds, total N was more than 80% NO_3. Some forms of N showed a weak negative correlation with the percentage of forest, because of the negative correlation between the percentage of cropland and forest among the watersheds. No other land use variables were correlated with forms of N, and adding a second land-use regressor after percentage of cropland did not significantly improve the regressions for N species.

Table 3. Annual water discharge (cm/yr, 1 cm = 100 m^3/ha) during the 1-yr study and percent yield of precipitation inputs from study watersheds. Precipitation input was 104 cm for the Rhode River watersheds, 96 cm for the inner Delmarva, 95 cm for the central, and 106 cm for the outer Coastal Plain watersheds. The long-term average for annual precipitation is about 113 cm for these regions (Maryland State Climatologist).

Watershed	Discharge	Yield
	cm	%
Innter Coastal Plain		
Rhode River		
101	23	22
102	22	21
103	20	19
108	14	13
109	14	13
110	14	13
111	17	16
Delmarva		
301	32	33
302	42	44
303	48	50
Central Coastal Plain		
304	27	29
305	34	35
306	24	25
310	35	37
Outer Coastal Plain		
307	11	10
308	29	27
309	31	29

Unlike N concentrations, P concentrations did not correlate with any land use, but differed among watershed clusters. Total P concentrations of the Rhode River watersheds were significantly higher than those of the inner or outer Coastal Plain watersheds on the Delmarva peninsula, and total P concentrations of the central Coastal Plain watersheds were significantly higher than those of the outer Coastal Plain watersheds ($P <$ 0.05, ANOVA of log-transformed flow-weighted mean concentrations, followed by Tukey comparison of means).

Concentrations of P species correlated strongly with concentrations of particulate matter (Fig. 6), reflecting the predominance of particulate forms of P (Table 4). In grab samples, median percentages of dissolved PO_4 in total PO_4 ranged from only 11 to 37%, and median percentages of dissolved organic P in TOP ranged from only 8 to 29% (Table 4). In contrast, total NH_4, TON, and TOC were predominately dissolved (Table 4). It is not clear why concentrations of P species and particulate matter were higher for the central Coastal Plain and Rhode River watersheds (Fig. 6). In those watersheds, total PO_4 made up the majority of total P (56–76%), but it was less than half of the total P in most other watersheds.

Since different factors influence N and P concentrations, the ratio of N/P concentrations in stream water differed widely among the watersheds (Table 5) but was not clearly correlated with any particular land use. Atomic N/P ratios were highest (>120) for the outer Coastal Plain watersheds with 41 and 46% cropland. For these watersheds, the ratios of inorganic N/inorganic P were higher than the ratios of total N/total P. Stream water from these watersheds had unusally high NO_3 (Fig. 4) and unusually low P and particulate matter (Fig. 6) concentrations. Atomic N/P ratios were lowest (<16) for the Rhode River watersheds. For the Rhode River watersheds, the ratios of inorganic N/ inorganic P were even lower than the ratios of total N/total P. Stream water from the Rhode River watersheds had unusually high P and particulate matter concentrations (Fig. 6).

Concentrations of other constituents in stream water differed among watersheds but did not correlate with land use. For example, pH and alkalinity were highest in streams of the central Coastal Plain, and lowest in streams draining the mostly forested watersheds of the outer Coastal Plain and the Delmarva inner Coastal Plain (Table 6). Dissolved silicate concentrations were

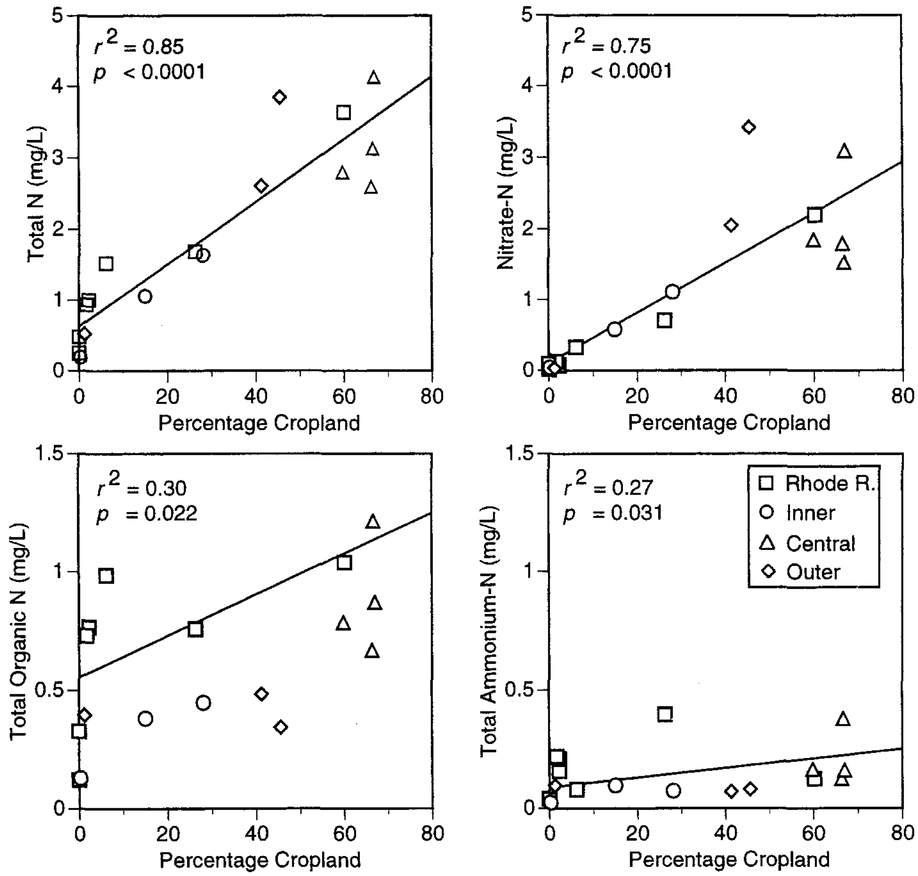

Fig. 4. Flow-weighted mean concentrations (mg N/L) of total N, dissolved NO_3, total NH_4, and TON vs. the percentage of cropland in the watersheds. Means are for 1 yr of weekly integrated samples. Different symbols represent different watershed clusters.

lowest in streams of the Delmarva inner Coastal Plain, and in the stream draining the mostly forested watershed of the outer Coastal Plain. The highest TOC concentration was observed in the stream draining the mostly forested watershed of the outer Coastal Plain. That watershed (307) had tea-colored water, indicating high concentrations of dissolved humic substances.

We calculated the discharge of materials by multiplying their flow-weighted annual mean concentrations by the annual water discharge. However, we did not use our own measurements of water discharge for this calculation because the observed relationship between water discharge and watershed size (Table 3) would introduce a bias. Also, errors in measuring water discharge would increase the variance in the calculated material discharge. Therefore, we based our calculations of material discharges on long-term mean rates of water discharge (Darling, 1962) reported for watersheds near our study watersheds (see discussion).

DISCUSSION

Water Discharge

Long-term means of water discharge rates for watersheds near our study sites (Darling, 1962, Table 7) were generally higher than the rates of discharge from our study watersheds (Table 3). The difference may be partly due to lower than average precipitation during our study (Table 3). However, the size of the watershed also seems to affect the discharge because discharge was usually less for the smaller watersheds we studied. Discharges from the largest watersheds we studied (Table 3) were similar to those from similar-sized watersheds reported by Darling (1962, Table 7).

We assume that the boundaries of our study watersheds coincide with the topographically defined catchment of surface runoff. However, groundwater flow can

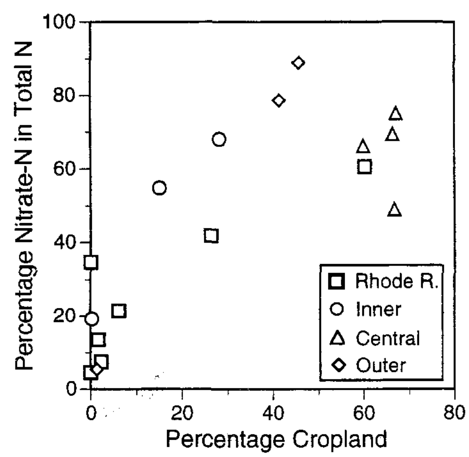

Fig. 5. Percentage of total N composed of dissolved NO_3 vs. the percentage of cropland in the watersheds. Percentages were calculated from flow-weighted mean concentrations (Fig. 4).

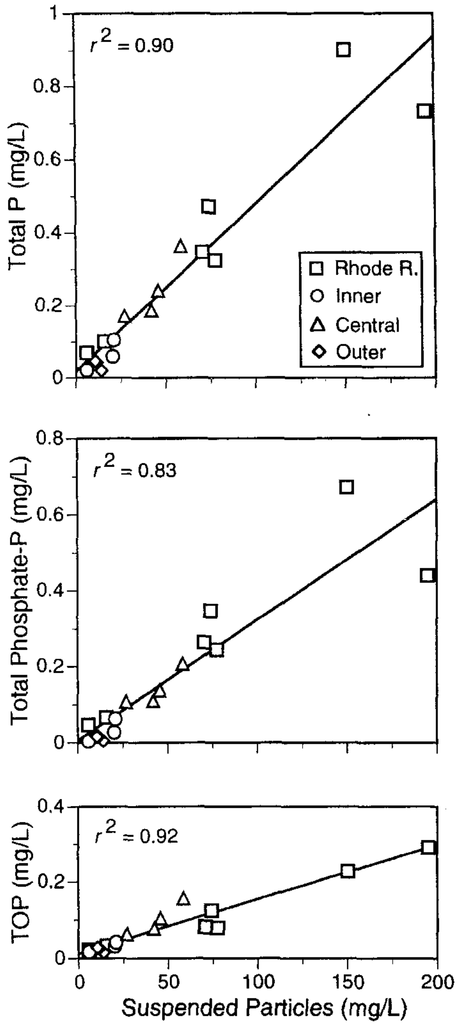

Fig. 6. Flow-weighted mean concentrations (mg P/L) of total P, total PO_4, and TOP vs. the flow-weighted mean concentrations of suspended particles (mg/L). Means are for 1 yr of weekly integrated samples. For all regressions, $p < 0.0001$.

cross these boundaries, so the true collection areas of streams become increasingly uncertain as the watershed areas decrease and the edge to area ratios increase. Groundwater loss probably accounts for the very low discharge and water yield from watershed 307, a very small watershed with sandy soils in the Outer Coastal Plain. However, groundwater loss may not be important for the small Rhode River watersheds because they are underlain by impermeable clay (Chirlin and Schaffner, 1977). For the Rhode River watersheds, evapotranspiration may increase relative to streamflow as watershed area decreases.

Compared to our measurements, the discharge rates reviewed by Darling (1962) are probably more representative of typical rates for the Coastal Plain, because they cover a longer time period and are for watersheds with larger areas than our study watersheds. Therefore, we used the long-term regional mean rate of water discharge in calculating discharge of materials from our watersheds. Discharges of materials per area from each study watershed were calculated by multiplying the flow-weighted mean concentrations for each watershed by the mean water discharge per area for the watershed's region (Table 7). In most cases, this results in higher estimates of material discharge than would be obtained from using our measurements of water discharge.

Table 5. Atomic ratios of total N to total P (TN/TP) and total inorganic N to total inorganic P (TIN/TIP) in discharges from the study watersheds.

Watershed	TN/TP	TIN/TIP
Inner Coastal Plain		
Rhode River		
101	6.4	2.0
102	7.1	3.4
103	2.8	1.0
108	11	8.4
109	8.9	8.6
110	11	4.9
111	8.0	5.8
Delmarva		
301	20	36
302	62	95
303	23	24
Central Coastal Plain		
304	34	40
305	33	41
306	19	20
310	38	53
Outer Coastal Plain		
307	55	51
308	190	450
309	120	270

Nitrogen and Phosphorus Discharges

We found dramatic differences in watershed discharges related to both land use and location within the Coastal Plain. 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 discharge (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 the effects of the geochemistry and erodibility of sediments in the watershed (Grobler and Silberbauer, 1985; Vighi et al., 1991; Dillon and Kirchner, 1975; Rekolainen, 1990).

Table 4. Median percent dissolved nutrient in total nutrient with the 25th and 75th percentiles in parentheses. Data are from grab samples taken at different stages of stream flow throughout the year.

	Median percent dissolved				
Region	PO_4	Organic P	NH_4	Organic N	Organic C
Inner: Rhode River	19 (8–33)	15 (3–44)	80 (67–90)	38 (15–63)	50 (26–74)
Inner: Delmarva	11 (2–29)	11 (4–34)	62 (52–79)	70 (63–91)	78 (57–91)
Central	37 (26–59)	8 (3–19)	72 (55–87)	68 (37–86)	78 (58–92)
Outer	12 (7–33)	29 (2–70)	71 (58–84)	79 (69–97)	74 (53–86)

Table 6. Flow-weighted annual mean concentrations. Alkalinity (µeq $CaCO_3$/L) and pH were measured in weekly grab samples taken throughout the 1 yr period. Dissolved silicate (mg Si/L) and TOC (mg organic C/L) were measured in composite samples pumped by the automated samplers and collected weekly. The weekly flow was used as a weighting factor in calculating the means.

Watershed	pH	Alkalinity	Silicate	TOC
		µeq/L	mg Si/L	mg C/L
Inner Coastal Plain				
Rhode River				
101	6.15	145.0	6.05	8.18
102	6.47	209.0	5.35	10.4
103	6.55	251.0	9.89	9.48
108	6.23	143.0	9.47	6.41
109	5.85	52.3	9.44	10.3
110	5.72	81.6	5.20	6.89
111	5.53	38.5	–	2.10
Delmarva				
301	4.52	0.22	3.02	3.64
302	6.33	120.0	3.96	6.50
303	6.35	147.0	4.36	6.73
Central Coastal Plain				
304	7.42	1010.0	6.83	7.66
305	7.07	605.0	6.00	8.74
306	6.82	585.0	6.78	11.2
310	6.88	559.0	6.07	9.41
Outer Coastal Plain				
307	4.01	0.00	3.40	12.8
308	6.15	87.3	6.50	4.02
309	6.17	138.0	7.80	7.95

Phosphorus fluxes are difficult to quantify because P is strongly associated with suspended particles transported mainly during episodic high flows (Walling and Webb, 1985; Kronvang, 1992), but we were able to sample episodic fluxes with our automated samplers. We estimated P discharge from the flow-weighted mean concentrations in stream water and the long-term regional average rate of water discharge (Table 8). Phosphorus discharge ranged from 0.073 to 0.47 kg ha^{-1} yr^{-1} for the inner Delmarva and outer Coastal Plain watersheds, 0.61 to 1.3 kg ha^{-1} yr^{-1} for the central Coastal Plain and 0.30 to 4.0 kg ha^{-1} yr^{-1} for watersheds of the Rhode River. By comparison, other measurements of P discharges reviewed by Beaulac and Reckow (1982) 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. It is not clear why there were systematic differences in P concentrations and discharges among our different clusters of watersheds. Phosphorus discharges from the outer Coastal Plain watersheds were among the lowest we observed despite the high P enrichment of soils from applications of poultry manure in Sussex county (Mozaffari and Sims, 1994).

Most of the variability in the concentrations of forms of N could be explained by the proportion of cropland in our watersheds. Thus, the discharge of N is also related to the proportion of cropland. This relationship can be used to infer the discharge of N per ha of cropland or noncropland. We estimated discharge of N using flow-weighted mean concentrations in stream water and the long-term regional average rate of water discharge (Table 8). Then, from a regression of N discharge against the percentage of cropland, we calculated N discharge at 0% cropland and at 100% cropland. By this estimation, cropland discharges 18 kg N ha^{-1} yr^{-1} and noncropland discharges 2.9 kg N ha^{-1} yr^{-1}. These rates are consistent with those used by Fisher and Oppenheimer (1991) to estimate N inputs to Chesapeake Bay: 20 kg N ha^{-1} yr^{-1} for cropland, 5.8 kg N ha^{-1} yr^{-1} for pasture, and 1.4 kg N ha^{-1} yr^{-1} for forest. Other measurements of N discharges, reviewed by Beaulac and Reckow (1982), covered a broad range that encompassed our estimates. However, their averages for row crops (9 kg ha^{-1} yr^{-1})

Table 7. Average annual stream discharges (cm/yr, 1 cm = 100 m^3/ha) and drainage areas (km^2) from different regions of the Coastal Plain of Maryland (Darling, 1962). Data are averages for 5 to 26 yr periods ending in the late 1950s (Darling, 1962).

Region, Stream	Area	Discharge
	km^2	cm/yr
Inner Coastal Plain, near Rhode R.		
North R.	22	44
Bacon Ridge	18	52
Patuxent R. at Largo	78	36
Average		44
Inner Coastal Plain, Delmarva		
Jacobs Cr. at Sassafras	14	32
Big Elk Cr. at Elk Mills	136	46
Little Elk Cr. at Childs	69	49
Northeast Cr. at Leslie	63	51
Average		45
Central Coastal Plain, Delmarva		
Choptank R. at Greensboro	293	39
Tuckahoe Cr.	221	38
Sallie Harris Cr.	21	35
Chester R. at Millington	58	36
Morgan Cr. at Kennedyville	27	32
Southeast Cr. at Church Hill	32	35
Average		36
Outer Coastal Plain, Delmarva		
Wicomico Basin at Salisbury	51	42
Nanticoke R. near Hebron	32	25
Chicamacomico R.	39	38
Average		35

Table 8. Concentrations (mg/L) and discharges (kg ha^{-1} yr^{-1}) of total P and total N for the study watersheds. Concentrations are flow-weighted mean values for each watershed averaged over the 1 yr study. Discharges per ha are calculated by multiplying the concentrations by the regional long-term annual mean water discharges per ha for nearby watersheds (Darling, 1962). These mean water discharge rates are 44 cm for the area near the Rhode River, 45 cm for Delmarva inner Coastal Plain watersheds, 36 cm for central Coastal Plain, and 35 for the outer Coastal Plain (Table 7).

	Total P		Total N	
Watershed	Concentration	Discharge	Concentration	Discharge
	mg/L	kg ha^{-1} yr^{-1}	mg/L	kg ha^{-1} yr^{-1}
Inner Coastal Plain				
Rhode River				
101	0.35	1.5	1.0	4.4
102	0.47	2.1	1.5	6.7
103	0.73	3.2	0.94	4.1
108	0.32	1.4	1.7	7.4
109	0.90	4.0	3.6	16
110	0.10	0.44	0.48	2.1
111	0.068	0.30	0.25	1.1
Delmarva				
301	0.021	0.093	0.19	0.86
302	0.059	0.26	1.6	7.4
303	0.10	0.47	1.1	4.8
Central Coastal Plain				
304	0.17	0.61	2.6	9.4
305	0.19	0.67	2.8	10
306	0.36	1.3	3.1	11
310	0.24	0.86	4.1	15
Outer Coastal Plain				
307	0.021	0.073	0.52	1.8
308	0.044	0.15	3.8	13
309	0.046	0.16	2.6	9.1

and mixed agricultural land (15 kg ha^{-1} yr^{-1}) were somewhat lower than our estimate for cropland.

Discharge rates estimated by extrapolating regressions should be interpreted cautiously. Although our extrapolation suggests that pure cropland discharges 18 kg N ha^{-1} yr^{-1}, the discharge at the edge of the crop field could be much higher if adjacent noncroplands trap N released by the cropland (Jordan et al., 1986a). The discharges 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 noncropland. Lands selected for crops had different characteristics historically than other lands, and these differences may affect N discharges even in absence of cultivation.

Comparing Nitrogen Discharges to Anthropogenic 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, pastures, and nonagricultural lands 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; Jordan et al., 1995). Agricultural lands also receive N from applications of N fertilizer and from N_2-fixing crop plants. We consider N_2 fixation by crop plants an anthropogenic input because it is fostered by human activity. Nitrogen 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. Unlike fertilizer N or N fixed by crop plants, livestock waste N is not a new addition to agricultural N flux, but it can be an important input of N to croplands. We account for all the major inputs and outputs in our calculation of net anthropogenic N input to particular land use types.

Data for our calculation of anthropogenic N inputs came from several sources. We used county-level estimates of wet atmospheric deposition compiled by the U.S. Geological Survey (Puckett, 1994; Larry Puckett, 1994, 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 areas of croplands and crop harvests within counties came from the 1987 census of agriculture (Bureau of the Census, 1993). Crop harvests were converted to units of N as described by Jordan and Weller (1996). Dinitrogen fixation by crop plants was estimated from the areas of different crops (Bureau of the Census, 1993) and typical rates of N_2 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). Nitrogen 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 (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 NH_3 before and after application to croplands. Typically, 10 to 40% 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% loss of N from livestock waste.

Our calculations suggest that the net anthropogenic inputs of N to pastures and nonagricultural lands are similar (Table 9). Anthropogenic inputs to nonagricultural lands are due to atmospheric deposition that ranges from 9 to 13 kg N ha^{-1} yr^{-1}. By comparison, net inputs to pastures range from -22 kg N ha^{-1} yr^{-1} (a net loss) to 24 kg N ha^{-1} yr^{-1}. The wide range of rates for pastures is due to the uncertainty about the amount of N loss from volatilization of NH_3 from livestock waste. For pastures, the estimated net removal of N by grazers was roughly balanced by the assumed N_2-fixation rate of pastures, 15 kg N ha^{-1} yr^{-1} (Table 9). The net N input to pastures was probably underestimated by assuming that fertilizer is applied only to cropland, but the similarity of net inputs to pastures and nonagricultural lands is consistent with our findings that N discharges from watersheds did not increase as the proportion of managed grassland (including pastures and hayfields) increased.

Croplands apparently receive much higher anthropogenic inputs of N than do pastures and nonagricultural lands (Table 10). Inputs to croplands differ among counties due to differences in fertilizer application and in production of livestock waste. We estimated fertilizer N application to croplands in different counties ranging from 58 to 139 kg N ha^{-1} yr^{-1} and production of waste

Table 9. Anthropogenic inputs of N for pastures and nonagricultural lands (kg ha^{-1} yr^{-1}) in the counties that include the study watersheds. Units are per ha of pasture or nonagricultural land. Net N input to nonagricultural land is only from wet and dry atmospheric deposition, which we estimate as twice the amount of wet deposition. Livestock waste is only that which was deposited in pastures by grazing livestock (see text). The range of values for livestock waste reflects alternative assumptions of 50% loss or no loss of N due to NH_3 volatilization. Grazed N is estimated uptake of N by grazing livestock. The net input to pastures is the sum of atmospheric deposition, livestock waste (either low or high estimates), and N_2 fixation in pastures (Jordan and Weller, 1996), minus the N removed by grazing. The Delmarva watershed in New Castle County is number 302 (Table 1, 2), 301 and 303 are in Cecil County.

Region, county, state	Atmos. deposition	Livestock waste	N_2 fixation in pasture	Grazed N	Net input to pastures
Inner, Rhode R.					
Anne Arundel, MD	12	17–33	15	36	8–24
Inner, Delmarva					
New Castle, DE	12	14–28	15	36	5–20
Cecil, MD	13	27–54	15	70	−15–12
Central					
Queen Annes, MD	12	30–60	15	79	−22–8.1
Outer					
Sussex, DE	9	32–64	15	78	−22–11

N per ha of cropland ranging from 8 to 246 kg N ha^{-1} yr^{-1} (Table 10). Sussex county, Delaware, on the Outer Coastal Plain, had by far the highest application of livestock waste per ha of cropland and had the lowest input of fertilizer N (Table 10). In Sussex county, intensive production of broiler chickens leads to high rates of application of chicken manure to croplands (Sims and Wolf, 1994). Manure application reduces the need of additional N fertilizer, but Sussex county still had the highest estimated input of N per ha of cropland, 160 to 283 kg N ha^{-1} yr^{-1}. Net inputs in other counties ranged from 65 to 138 kg N ha^{-1} yr^{-1} (Table 10).

We calculated the net anthropogenic input of N to each watershed by multiplying the areas of croplands, pastures, and nonagricultural lands (Table 1) by the rates of input for each particular land use type in the appropriate county (Tables 9 and 10). We assume that all managed grasslands (which include pastures, Table 1) receive the same net N input as pastures. However, this assumption is not critical because our estimates of inputs to pastures are similar to our estimates of inputs to nonagricultural lands (Tables 9 and 10).

We compared N discharges (Table 8) to net anthropogenic N inputs. As expected, N discharge increased as the anthropogenic input of N to the watershed increased (Fig. 7). However, the amount of N discharged was generally less than a third of the net anthropogenic input, even if we assume that half of the livestock waste N is lost N due to NH_3 volatilization. If we assume no loss of livestock waste N, then the outer Coastal Plain watersheds with more than 40% cropland appear to discharge an especially small proportion of the anthropogenic input (Fig. 7). This is because the production of livestock waste is such a large component of the input to croplands in the Sussex county which includes our outer Coastal Plain watersheds. Some error in our estimates of anthropogenic input may come from assuming that the average N input rates for croplands within a county can be applied to the croplands within our particular study watersheds. However, despite imprecision in our estimates, it seems clear that only a fraction of the net anthropogenic N input is released in watershed discharges. Most of our study watersheds discharged between 15 and 30%, and some discharged <10% (Fig. 7) of the estimated net anthropogenic N input. This is consistent with findings that riverine discharges account for less than one-third of anthropogenic N inputs at spatial scales of whole river basins, such as the Mississippi drainage (Jordan and Weller, 1996; Howarth et al., 1997).

What is the fate of most of the anthropogenic N input to the watersheds if it is not discharged in streams or rivers? It must be either stored in groundwater, soil organic matter, or biomass, or converted to gaseous forms and released to the atmosphere. Anthropogenic N dispersed via water-borne or atmospheric transport may accumulate as organic N in forest soil and wood. Forests in the USA (Turner et al., 1995) and globally are accumulating organic matter, possibly in response to concurrent increases in atmospheric CO_2 and in depo-

Table 10. Anthropogenic inputs of N for croplands (kg ha^{-1} yr^{-1}). Units are per ha of cropland. Livestock waste is that which was not deposited in pastures by grazing livestock and therefore available for application to croplands (see text). The range of values for livestock waste reflects alternative assumptions of 50% loss or no loss of N due to NH_3 volatilization. N_2 fixation is based on the areas of crops grown and average N_2 fixation rates for particular crops (Jordan and Weller, 1996). The net input is the sum of atmospheric deposition, fertilizer, livestock waste, and N_2 fixation, minus the harvested N.

Region, county, state	Atmos. deposition	Fertilizer	Livestock waste	N_2 fixation by crops	Harvest	Net input
Inner, Rhode R.						
Anne Arundel, MD	12	139	14–28	36	77	124–138
Innter, Delmarva						
New Castle, DE	12	100	8–16	32	87	65–74
Cecil, MD	13	97	27–54	40	85	92–120
Central						
Queen Annes, MD	12	85	14–28	32	66	77–90
Outer						
Sussex, DE	9	58	123–246	45	75	160–283

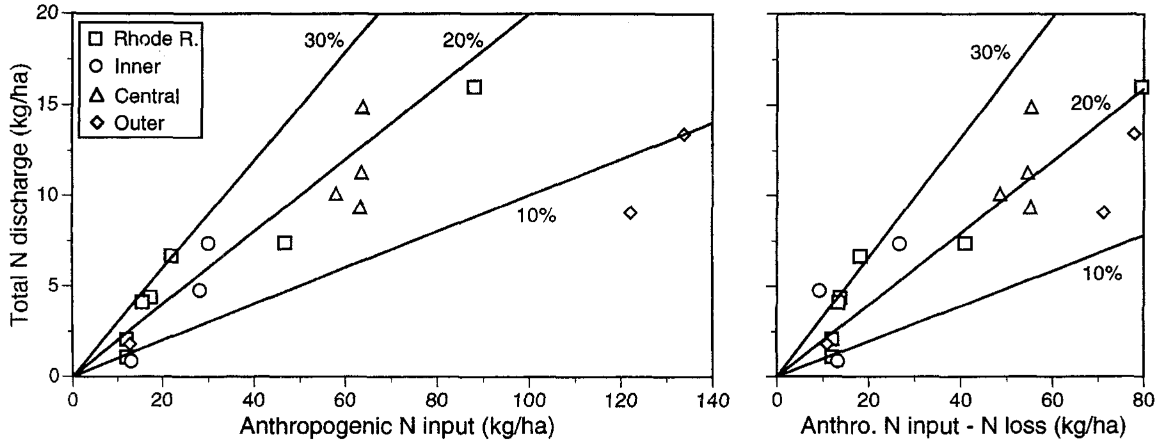

Fig. 7. Annual discharge of total N (kg/ha per yr) vs. net anthropogenic input of N (kg/ha per yr) to the watersheds. Anthropogenic inputs are calculated by multiplying average rates of input for croplands (Table 10) and other lands (Table 9) by the areas of these land types in each watershed (Table 1). Lines indicate discharges of 10, 20, and 30% of the net anthropogenic inputs. On the righthand graph, net anthropogenic inputs were lowered to account for possible 50% loss of N from livestock waste due to NH_3 volatilization. Discharge was calculated from flow-weighted mean concentrations (Table 8) and regional mean water discharge rates (Table 7).

sition of N (Schindler and Bayley, 1993). Many studies show increasing trends in NO_3 concentration in groundwater in Europe (Strebel et al., 1989) and North America (Power and Schepers, 1989), but the amount of N accumulating in groundwater and its rate of subsequent release to surface waters are generally not well known. A study of watersheds between our inner and central Coastal Plain sites on the Delmarva peninsula measured average residence times of more than 20 yr for groundwater and concluded that much of the NO_3 leached from fertilized croplands has yet to emerge in streams (Bohlke and Denver, 1995). This study also found that some of the groundwater NO_3 was converted to N_2 by denitrification in the groundwater (Bohlke and Denver, 1995). Denitrification can also produce nitrous oxide and nitric oxide gases. 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 N_2 fixation. Nitrous oxide contributes to global warming (Abrahamson, 1989; Lal and Holt, 1991), and depletion of stratospheric ozone (Bolin et al., 1983), while nitric oxide contributes to acid deposition (Cicerone, 1989).

In our study watersheds, riparian (streamside) forests are one possible N sink. Agricultural fields on the Coastal Plain are typically located on well drained uplands above poorly drained riparian forests (Gilliam and Skaggs, 1988; Correll, 1991). These riparian forests can retain 70 to 90% 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). The mechanisms of N removal by riparian forests are not well understood, but much of the N removal may be due to denitrification (Lowrance, 1992; Haycock and Pinay, 1993; Weller et al., 1994). Studies of riparian forests in our Rhode River watershed 109 (Peterjohn and Correll, 1984, 1986) and Delmarva watershed 304 (Jordan et al., 1993) found that shallow aquicludes forced groundwater to flow laterally through forest soils where NO_3 was removed. In contrast, riparian forests had little effect on dissolved NO_3 in other Delmarva watersheds where groundwater flow was too deep to pass through the rooting zone before emerging in the streams (Bohlke and Denver, 1995).

Effects on Eutrophication

The N, P, dissolved silicate, and TOC that are discharged by watersheds contribute to eutrophication of coastal waters. Judging from concentration data (Table 6), discharges of dissolved silicate and TOC did not differ among watersheds as much as the discharges of N and P (Table 8). Nitrogen and P were discharged in widely different proportions by different watersheds (Table 5). Thus, the characteristics of the watershed may promote either N or P limitation of phytoplankton growth in estuarine receiving waters. Discharges from the outer Coastal Plain watersheds, which had atomic N/P ratios above 50 (Table 5), would promote P limitation of phytoplankton growth in the receiving waters because the typical N/P ratio in phytoplankton biomass is only 16 (Redfield, 1958). 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, the discharges from the Rhode River watersheds had N/P ratios <16 (Table 5), which might promote N limitation in the Rhode River estuary.

Particulate and dissolved forms of nutrients differ in N/P ratio. For the Rhode River watersheds, N, P ratios were below 9 for the combined total of both particulate and dissolved inorganic forms (Table 5). However, the dissolved inorganic forms of N and P, which are immediately available for phytoplankton uptake, are discharged at an N/P ratio of 26 from the Rhode River watershed (Jordan et al., 1991a). Thus, the potential availability of particulate nutrients to phytoplankton also influences whether N or P may become limiting. Mass balances of nutrients in the Rhode River estuary suggest that particulate PO_4 from watershed discharge is rapidly converted to dissolved PO_4 in the upper estuary, increasing the supply of dissolved inorganic P and promoting N limitation (Jordan et al., 1991a). Since P in particulate forms can become available to phytoplankton, it is important to quantify discharges of particulate P from watersheds. Furthermore, since discharge of particulate P is very episodic (Jordan et al., 1986b), it is advantageous to use continuous automated sampling to measure it.

Differences in nutrient discharges among watersheds can lead to variability in the distributions of nutrients and phytoplankton in near-shore waters of Chesapeake Bay. For example, the difference in N/P ratios in discharge from the Rhode River watershed compared to discharge from the Susquehanna River leads to sharp gradients in the ratios of N and P concentrations in the Rhode River subestuary (Jordan et al., 1991a, b), which affects phytoplankton growth along the gradients (Gallegos, 1992). It seems likely that the dramatic differences in nutrient discharges among other Coastal Plain watersheds should likewise have effects on phytoplankton in the many subestuaries and embayments that line the Chesapeake. Therefore, knowledge of the factors that affect discharges from Coastal Plain watersheds is needed for a better understanding of the ecology of the near-shore waters of Chesapeake Bay.

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