WATER RESOURCES RESEARCH, VOL. 35, NO. 8, PAGES 2513–2521, AUGUST 1999

Transport of nitrogen and phosphorus from Rhode River watersheds during storm events

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Abstract. We studied storm discharges of nitrate and dissolved and particulate forms of ammonium, organic N, phosphate, and organic P from four adjacent small watersheds of differing land use on the Atlantic Coastal Plain in Maryland. We used V-notch weirs and automated storm samplers to measure discharges and collect samples at flow intervals during 76 storms. The watershed aquifers are perched on an impervious clay layer slightly above sea level, so that combined groundwater and surface water discharges were measured at the weirs. The concentrations of particulate forms of organic N (PON), organic P (POP), and inorganic P (PPi) increased up to 3 orders of magnitude during storm events and usually peaked prior to the peak water discharge, while concentrations of dissolved forms of organic N (DON), organic P (DOP), inorganic P (DPi), and nitrate did not change very much. Dissolved and particulate ammonium (DNH4 and PNH4, respectively) concentrations increased up to fivefold in storm events but remained low compared to other N forms. The watershed with the most cropland discharged the highest concentrations of total N, PON, DNH4, nitrate, POP, and PPi. A forested watershed discharged the highest concentrations of DON, PNH4, and DOP. The watershed with the most grazed land discharged the highest concentration of DPi. PON and POP were the dominant forms of N and P in storm discharges from all watersheds. Concentrations of nitrogen were higher in spring and summer storms than in winter storms, but phosphorus concentrations were much higher in the summer storms than in spring or winter. The concentrations of PPi, POP, PON, DNH4, and PNH4 increased significantly with peak water discharge among storms, while concentrations of DPi, DOP, DON, and nitrate were not correlated with peak discharge. The ratios of TN/TP and TIN/TIP declined significantly with peak water discharge among storms.

1. Introduction

A large number of studies have measured the discharge of nitrogen and phosphorus from various watersheds. The usual focus has either been comparative effects of land use in a small region [e.g., *Cooper and Thomsen*, 1988; *Correll and Dixon*, 1980; *Hill*, 1978; *Hirose and Kuramoto*, 1981; *Jordan et al.*, 1997a, b] or differences in discharges among widely separated regions [e.g., *Beaulac and Reckhow*, 1982; *Frink*, 1991; *Jordan et al.*, 1997c; *Malmer and Grip*, 1994]. These studies have clearly established that land use, particularly intensive agriculture, has a strong influence on nutrient discharges. They have also shown that nutrient discharges from a given watershed vary seasonally in temperate regions. The evidence seems fairly good that there are also significant differences in nutrient discharges from a given land use in different regions, perhaps because of geological and climatic differences. Relatively few studies have reported the patterns of change in concentrations and fluxes of the various forms of nitrogen and phosphorus in watershed discharges during a storm event [e.g., *Burt and Arkell*, 1987; *McDiffett et al.*, 1989; *O'Brien et al.*, 1993]. These studies have shown that during individual storm events concentrations of individual forms of a nutrient span a broad range during the storm but are not in synchrony with the hydrograph, usually reaching peak concentrations before peak water discharge.

Our study provides a unique perspective because the watersheds we studied were small, paired first- and second-order streams with relatively simple land use compositions, but they have essentially the same weather and soils. We also studied many storm events with a wide range of intensity. Such an analysis requires many years of data from the same watersheds. The watersheds were continuously monitored for discharge with V-notch weirs which included volume-integrating, flow-proportional storm event samplers. It is our objective to define the effects of variations in storm intensity, magnitude, and timing on nutrient discharges from forested, cropped, grazed, and mixed-land-use watersheds on the inner mid-Atlantic Coastal Plain of North America.

2. Methods

2.1. Site Description

The watersheds studied are all subwatersheds of the Rhode River, a tidal tributary to the Chesapeake Bay in Maryland, United States of America (38°51′N, 76°32′W). The Rhode River is within the inner Atlantic Coastal Plain. The watershed has sedimentary soils from the Pleistocene Talbot formation at low elevations on the eastern part of the watershed, Eocene Nanjemoy formation soils at low elevations farther west, Miocene Calvert formation soils at intermediate elevations, and Pleistocene Sunderland formation soils at the highest eleva-

Paper number 1999WR900058.

Table 1. Characteristics of Rhode River Subwatersheds

Water-shed	Stream Order	Area,[a] ha	Mean Slope,[b] %	Mean Discharge,[c] mm/yr	Land Use[a] Forest, %	Row Crops, %	Pasture and Hay Fields, %	Residential	Old Fields, %
101	2	226	7.2	337	38	10	27	6	19
109	1	16.3	5.4	240	36	64	0	0	0
110	1	6.3	8.3	182	100	0	0	0	0
111	1	6.1	10.8	196	27	0	73	0	0

[a] *Correll* [1977].
[b] *Correll et al*. [1984].
[c] *Correll et al*. [1999].

tions [*Kirby and Matthews*, 1973]. The soils are fine sandy loams, and the mineralogy of the soils is fairly uniform, with a high level of montmorillonite and quartz, intermediate levels of illite and kaolinite, and low levels of gibbsite, chlorite, potassium feldspar, and plagioclase [*Correll et al*., 1984]. Bedrock is about 1000 m below the surface, but the Marlboro Clay layer forms an effective aquiclude slightly above sea level throughout the watershed [*Chirlin and Schaffner*, 1977]. Each subwatershed has a perched aquifer so that overland storm flows, interflow, and groundwater discharges all move to the channel above the weir.

The slopes of the of the four watersheds average between 5 and 11%. The study watersheds ranged in size from 6.1 to 226 ha and differed in land use (Table 1). Three watersheds were drained by first-order streams. One (110) was completely forested, another (109) was primarily row cropped, and one (111) was primarily rotationally grazed pasture. The other watershed (101) was drained by a second-order stream and had mixed land use. For more detailed descriptions of the site, see *Correll* [1981] and *Correll and Dixon* [1980].

2.2. Sampling

Discharges of water from each watershed were measured with sharp-crested V-notch weirs, whose foundations were in contact with the Marlboro Clay aquiclude [*Correll*, 1977]. All weirs were 120° notches, except for watershed 111, which was 150°. Each weir had an instrument building and a stilling well. Depths were measured to the nearest 0.3 mm with floats and counterweights and were recorded every 5 min.

Each weir was equipped with two automated samplers. One sampler composited stream water aliquots continuously, taken every 154 m^3 of flow for watershed 101 and every 77 m^3 of flow for the other watersheds, and these volume-integrated samples were collected weekly [*Correll*, 1981]. The second sampler was turned on by the rising hydrograph and took discrete, separate samples at flow intervals until the hydrograph returned to base flow or the sampler ran out of containers. Samples were taken from the stream channel upstream of the weir at flow intervals controlled by a Stevens, model 61R, flow meter, and the time of sampling on the hydrograph was recorded. Samples were collected within 24 hours and returned to the laboratory for processing. A total of 76 storm/watershed events were measured from December 1976 through May 1990 (Table 2).

2.3. Sample Analyses

Sample aliquots were filtered through prewashed Millipore membrane filters (0.45 μm pore size). Filtered aliquots were analyzed for dissolved constituents, and particulate constituents were calculated as the difference between unfiltered and filtered aliquots. Total Kjeldahl N (TKN) was determined by digestion to ammonium with sulfuric acid, Hengar granules, and hydrogen peroxide [*Martin*, 1972]. The ammonium in the digestate was steam distilled and analyzed by Nesslerization [*Am. Public Health Assoc*. (*APHA*), 1989]. Ammonium was also determined in undigested aliquots by oxidation to nitrite with alkaline hypochlorite [*Strickland and Parsons*, 1972] and analysis of the nitrite by reaction with sulfanilamide [*APHA*, 1989]. Total organic N was calculated by subtracting ammonium from TKN. The sum of nitrate and nitrite was measured by reducing nitrate to nitrite with cadmium amalgam and analyzing nitrite by reaction with sulfanilamide [*APHA*, 1989]. Total P was determined by digestion to orthophosphate with perchloric acid [*King*, 1932] and reaction with stannous chloride and ammonium molybdate [*APHA*, 1989]. Total phosphate was determined by acidification of the whole water samples to extract phosphate from particulates, filtration, and determination of

Table 2. Number of Storms, Mean and Range of Peak Discharges Measured in Each Season for Each of Four Watersheds

Season	Watershed 101* Storms	Mean	Range	Watershed 109† Storms	Mean	Range	Watershed 110‡ Storms	Mean	Range	Watershed 111§ Storms	Mean	Range
Winter	11	0.87	0.247–2.11	9	1.43	0.086–6.75	2	10.6	0.667–20.6	2	7.70	3.70–11.7
Spring	18	1.38	0.185–4.84	8	4.58	1.09–11.7	4	7.77	4.10–9.52	1	2.8	2.8
Summer	9	2.84	0.837–11.7	5	13.9	0.906–32.9	2	11.4	10.9–11.9	2	1.41	0.686–2.15
Fall	0	···	···	0	···	···	3	15.1	5.40–29.4	0	···	···
Total	38	1.58	0.185–11.7	22	5.40	0.086–32.9	11	11.0	0.667–29.4	5	4.21	0.686–11.7

Discharge values are given L ha^{-1} s^{-1}. Ellipsis indicates samples were not taken.
*Mixed land use is dominant for watershed 101.
†Row crops are dominant for watershed 109.
‡Forestation is dominant for watershed 110.
§Grazed land is dominant for watershed 111.

Table 3. Comparison of Rhode River Watershed Nutrient Concentrations in Storm Discharges and Base Flow Immediately Preceding and Following Storms

Parameter	Watershed 101 (Mixed Land Use)	Watershed 109 (Crops)	Watershed 110 (Forest)	Watershed 111 (Grazed)
		Storm Discharges		
Nitrate	380* ± 10.3 (364) 2	1680 ± 66.9 (113) 2, 4	136* ± 23.8 (67) 2, 4	310 ± 41.6 (20) 4
PNH4	56.1 ± 4.0 (208)	29.6 ± 4.2 (63)	50.9 ± 14.5 (9)	55.1* ± 10.1 (14)
DNH4	130 ± 4.7 (364) 2	160 ± 13.5 (107) 1, 4	68.7 ± 6.2 (67) 2, 4	100* ± 10.4 (20) 1
PON	2390* ± 228 (208) 1	2330* ± 380 (63) 2	992* ± 153 (9) 1, 2, 5	4110* ± 1140 (14) 5
DON	376* ± 12.5 (216) 1, 2, 6	450* ± 23.6 (104) 1, 4	496* ± 26.4 (67) 2, 5	283* ± 29.1 (20) 4, 5, 6
PPi	495* ± 39.6 (352) 2, 3	930* ± 182 (102) 4,6	61.8* ± 7.4 (67) 2, 4	191 ± 70.9 (13) 3, 6
DPi	18.4* ± 1.2 (275) 1	26.8* ± 2.1 (107)	22.9* ± 1.6 (67)	41.0 ± 7.9 (15) 1
POP	895* ± 91.0 (221) 1, 2	1780† ± 304 (102) 1, 4, 5	235* ± 21.0 (67) 2, 4	586† ± 200 (15) 5
DOP	16.7* ± 1.3 (221) 2	20.5† ± 1.9 (107) 4	40.0* ± 3.6 (67) 2, 4, 6	16.7† ± 3.2 (15) 6
		Base Flow Discharges		
Nitrate	267* ± 23.8 (106) 2	1420 ± 95.4 (106) 2, 4	46.0* ± 6.5 (95) 2, 4	328 ± 33.2 (87) 4
Total NH4	122 ± 14.9 (101) 1, 6	173.9 ± 31.6 (98) 2, 6	71.1 ± 6.7 (84) 1, 2, 3	48.4* ± 3.4 (85) 3, 6
TON	617* ± 58.1 (106) 2, 3	853* ± 216 (104) 1	345* ± 35.4 (87) 1, 2	313* ± 61.2 (88) 3
TPi	122* ± 14.6 (100) 2	221* ± 92.1 (94)	45.9* ± 6.4 (80) 2	85.4* ± 28.5 (78)
TOP	99.7* ± 11.4 (106) 2	488† ± 242 (104)	51.6* ± 5.4 (87) 2	63.7† ± 15.7 (88)

Concentrations are in micrograms N or P per liter ± 1 SE, with the number of samples in parentheses. Significant differences for the same parameter horizontally among subwatersheds are designated by 1, 3, or 5 for $P < 0.05$ or by 2, 4, or 6 for $P < 0.01$. Significance levels were determined by analysis of variance. In the case of storm nutrient concentrations, dissolved and particulate fractions were summed prior to comparison with base flow concentrations.

*There are significant differences between equivalent parameters vertically when $P < 0.05$.

†There are significant differences between equivalent parameters vertically when $P < 0.01$.

phosphate as above. Organic P was calculated by subtracting phosphate from total P.

2.4. Data Preparation

Discharge volumes were multiplied by nutrient concentrations to obtain instantaneous fluxes of various nutrient fractions, and these fluxes were integrated over the storm event to obtain overall discharge fluxes. Overall nutrient fluxes were divided by total water discharged to obtain volume-integrated, mean nutrient concentrations for each storm event. Watershed discharge data from the study watersheds (Table 1) were normalized by dividing by watershed area. For Table 3, base-flow volume-integrated sample data for 2 weeks prior to and 2 weeks subsequent to a storm or series of storms were summarized. These samples were only analyzed for total nutrient parameters rather than for dissolved and particulate fractions (e.g., total ammonium).

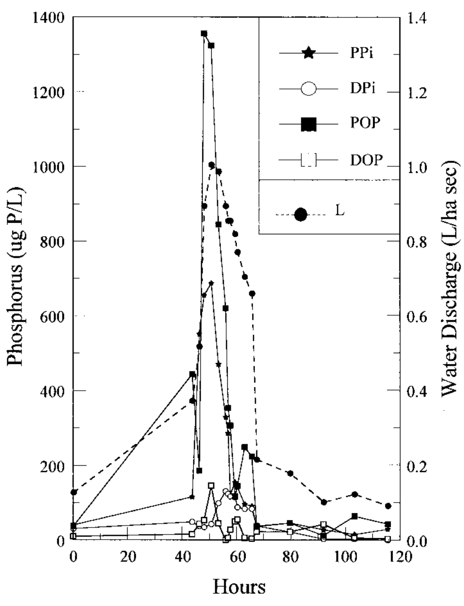

Figure 1. Water discharge rates and concentrations of various forms of phosphorus discharged from the mixed-land-use watershed (101) during a December storm. Abbreviations are as follows: DOP, dissolved organic P; POP, particulate organic P; PPi, particulate phosphate; and DPi, dissolved phosphate.

3. Results

3.1. Characteristic Storm Events

Typically, during a storm event the concentrations of particulate nutrients in a stream peak prior to the hydrograph peak. Such a storm event for watershed 101 is shown in Figure 1. This storm had a relatively moderate-sized peak discharge of about 1 L ha^{-1} s^{-1}. The largest phosphorus peak was for particulate organic P (POP), and the particulate phosphate (PPi) peak was about half as big, both peaking slightly prior to the hydrograph peak. Peaks for both dissolved phosphate (DPi) and dissolved organic P (DOP) were relatively small. The total fluxes of forms of phosphorus in this storm were 16.2, 9.6, 3.9, and 1.3 g P ha^{-1} for POP, PPi, DPi, and DOP, respectively. Eighty three percent of the total P discharged was particulate. In the case of larger storm events (e.g., Figure 2) the particulate peaks usually occur during the rising hydrograph. It should be noted that at the location of the particulate phosphorus peaks in this storm, the rate of water discharge had already exceeded the maximum for the storm in Figure 1.

For nitrogen, one form, particulate organic N (PON), usually constituted the bulk of the discharge and is the only form of nitrogen that increased dramatically in concentration during storm events. The PON also usually peaked well ahead of the hydrograph peak (e.g., Figure 3). The other forms of nitrogen measured, dissolved organic N (DON), dissolved and particulate ammonium (DNH4 and PNH4, respectively), and nitrate,

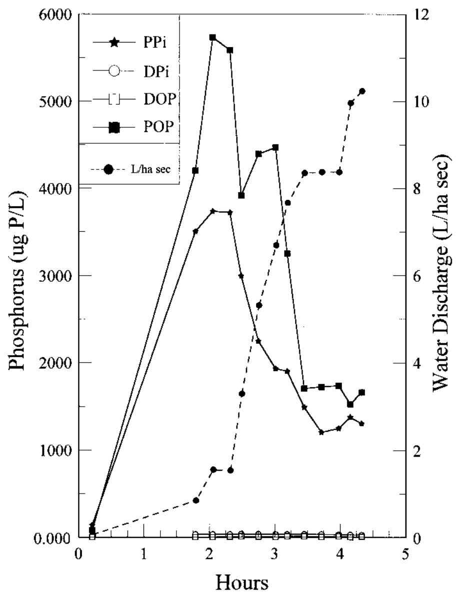

Figure 2. Water discharge rates and concentrations of various forms of phosphorus discharged from the mixed-land-use watershed (101) during the first part of a June storm. The discharge rate peaked at 11.7 L ha^{-1} s^{-1}. Abbreviations for forms of P are as in Figure 1.

increased little if at all during storm events. PON constituted 84% of the total N flux for the entire storm event in Figure 3.

3.2. Overall Comparisons Among Watersheds

On average, both the concentration of total N and its distribution among the forms of nitrogen differed among the studied watersheds (Figure 4). The concentrations of total N, PON, DNH4, and nitrate were highest from the cropland and, except for PON, were significantly higher than from forest or grazed land (Table 3). Nitrate was also a higher percentage of the discharges from cropland than from the other watersheds. Forest discharged the highest concentrations and percentage of DON and PNH4. PON was the dominant form of nitrogen discharged in storm events from all of the watersheds.

The differences in storm discharges of phosphorus among watersheds were larger (Figure 5) than was the case for nitrogen. POP constituted the largest fraction of the total P in storm events from all watersheds. The concentrations of POP and PPi in discharges from cropland were much higher than from the other watersheds, but the DPi concentration was higher from grazed land and constituted 14% of the total P. The DOP concentration was significantly higher from forest than cropland (Table 3) and constituted 13% of the total P. PPi was only 10 and 17% of the total P discharged from grazed land and forest, respectively.

3.3. Seasonal Comparisons Among Watersheds

When the storm events for the mixed-land-use watershed (101) are classified by season, the average summer storm resulted in higher concentrations of nitrogen in the discharges than in winter storms, primarily because of PON, which had significantly higher concentrations in the summer, while spring storms were intermediate (Figure 6). No fall storms were measured. PON was the largest fraction of the total N (73%) in the summer and was the lowest fraction in the winter (34%). In the winter, nitrate concentration and percentage of total N was greater than in the spring or summer. Both DNH4 and PNH4

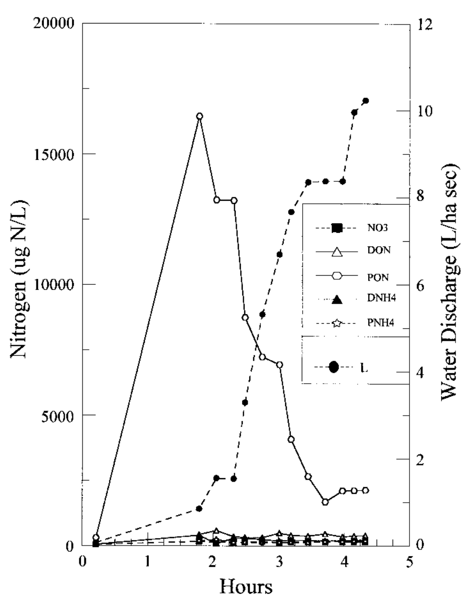

Figure 3. Water discharge rates and concentrations of various forms of nitrogen discharged from the mixed-land-use watershed (101) during the first part of a June storm. Abbreviations are as follows: PNH4, particulate ammonium N; DNH4, dissolved ammonium N; PON, particulate organic N; and DON, dissolved organic N.

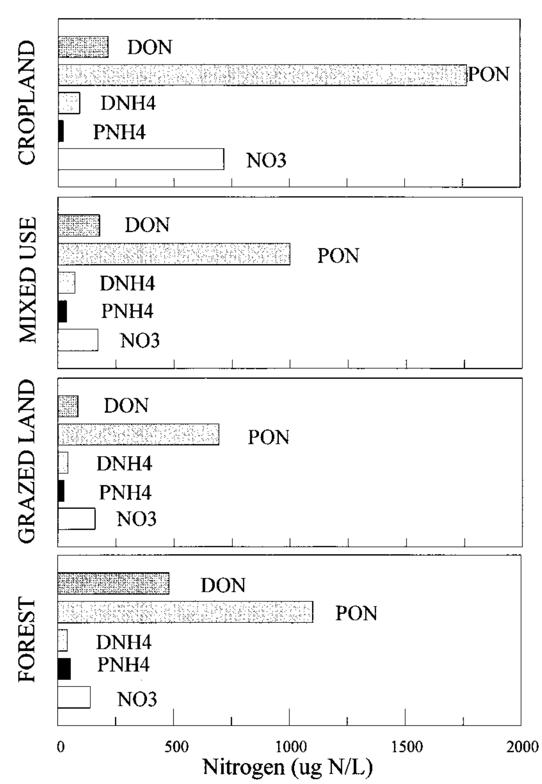

Figure 4. Comparisons of mean nitrogen concentrations in storm events from Rhode River watersheds. Abbreviations are as follows: DON, dissolved organic N; PON, particulate organic N; DNH4, dissolved ammonium N; and PNH4, particulate ammonium N.

were found in higher concentrations in the summer, but were lower percentages of the total N. For the cropland watershed (109) the seasonal pattern is somewhat different (Figure 7). Nitrate concentrations were a higher percentage in winter storms, constituting half of the total N. PON concentrations were highest in summer storms, constituting half of the total N. DNH4 and PNH4 concentrations were highest in the summer and, combined, constituted 7% of total N discharged during storms.

Total P discharge from the mixed-land-use watershed (101) was highest in summer storms and lowest in the winter (Figure 8). POP concentrations were significantly higher in the summer and constituted 60% of the total P discharge, while PPi constituted 56% of the total P discharge in the spring. DPi and DOP discharges were the highest proportion of the total in the winter (6 and 4%, respectively) but combined were only 1.2% of the total P in the summer. For the cropland, PPi constituted 54% of the total P in summer storms but constituted only 25% in winter storms (Figure 9). POP dominated the cropland discharges in spring and winter storms, while the combination of DPi and DOP only constituted a few percent of the total P discharge in storms.

3.4. Storm Intensity Effects

Large, intense storms discharged higher concentrations of particulate nutrients than smaller, less intense storms. Although there was considerable scatter in the data, variations in peak water discharge (Q) explained 64% of the variations in mean PPi concentration for storms on the mixed-land-use watershed (101) (PPi concentration = $265Q^{1.06}$ and $P < 0.00001$) (Figure 10). A similar relationship explained 61% of the variation in POP concentration for storms on the mixed-land-use watershed (101) (POP concentration = $353Q^{1.11}$ and $P < 0.01$). For the cropland watershed, variation in peak water discharge explained 93% of the variation in POP concentration (POP concentration = $314Q - 126$ and $P < 0.0001$) and 41% of the variation in PPi concentration (PPi concentration =

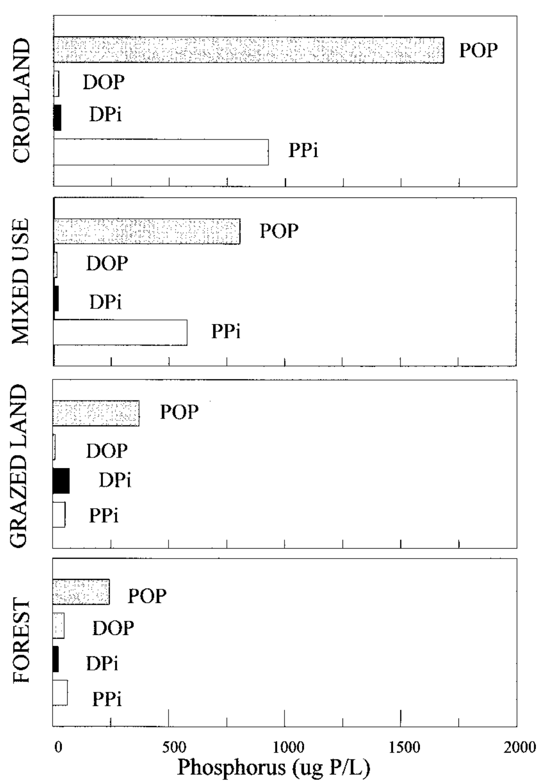

Figure 5. Comparisons of mean phosphorus concentrations in storm events from Rhode River watersheds. Abbreviations are as follows: POP, particulate organic P; DOP, dissolved organic P; DPi, dissolved phosphate; and PPi, particulate phosphate.

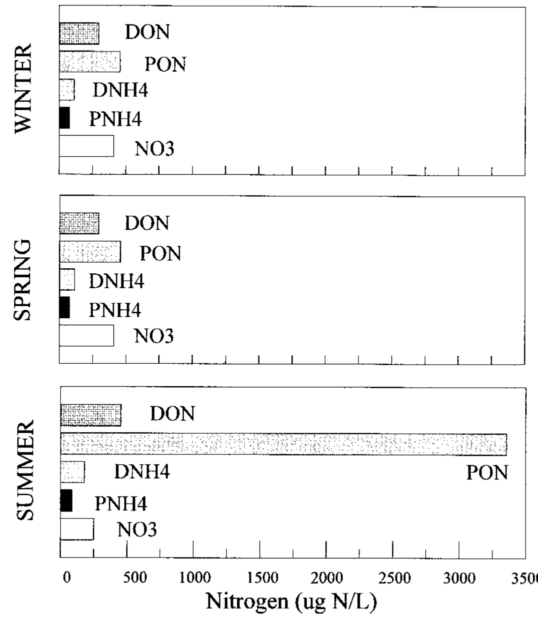

Figure 6. Seasonal comparisons of mean nitrogen concentrations in storm events from Rhode River mixed-land-use watershed (101). Winter is December, January, and February; spring is March, April and May; summer is June, July, and August. Abbreviations of N forms are as in Figure 4.

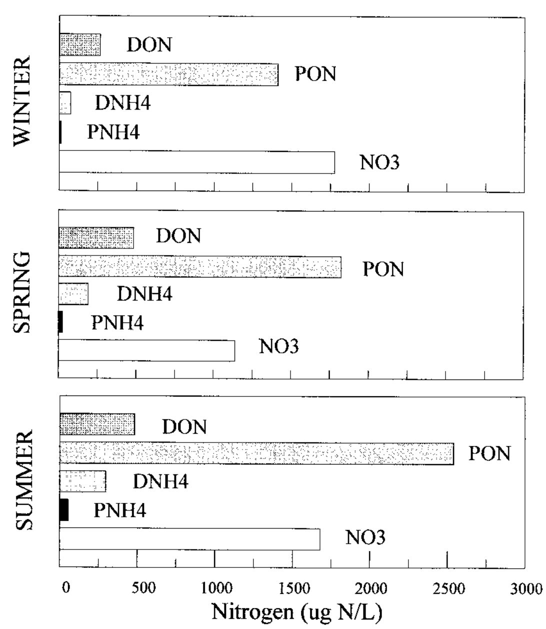

Figure 7. Seasonal comparisons of mean nitrogen concentrations in storm discharges from the cropland watershed (109). Abbreviations of N forms are as in Figure 4.

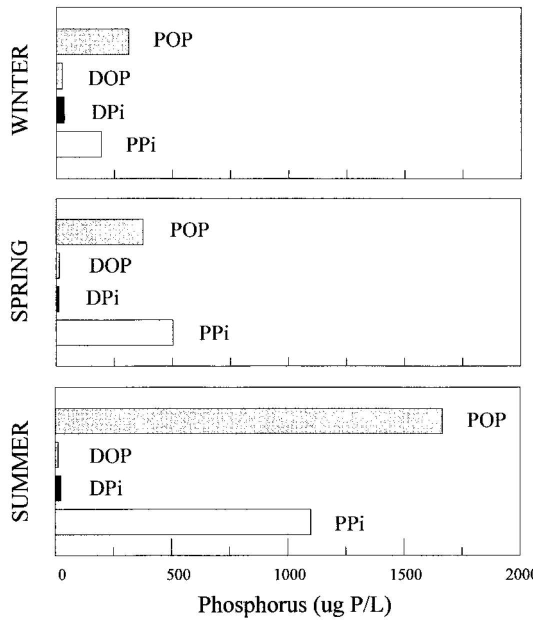

Figure 8. Seasonal comparisons of mean phosphorus concentrations in storm discharges from the mixed-land-use watershed (101). Abbreviations of P forms are as in Figure 5.

104Q + 242 and P = 0.002) (Figure 10). For the forested watershed, POP and PPi concentrations did not increase significantly with peak water discharge (Figure 10). Concentrations of DPi and DOP did not correlate with peak water discharge on any of the watersheds.

Variations in peak water discharge explained 50 and 83% of the variation in PON concentration in storms on mixed-land-use watershed and the cropland watershed, respectively ($PON_{101} = 1000Q^{1.01}$ and $P < 0.04$ and $PON_{109} = 167Q +$ 1280 and $P < 0.002$, respectively). Similarly, in the cropland watershed, peak water discharge explained 85 and 90% of the variation in DNH4 (DNH4 concentration = 11.75Q + 75 and $P < 0.001$) and PNH4 (PNH4 concentration = 1.90Q + 18 and $P < 0.001$) concentrations. Concentrations of DON and nitrate did not change very much with storm intensity.

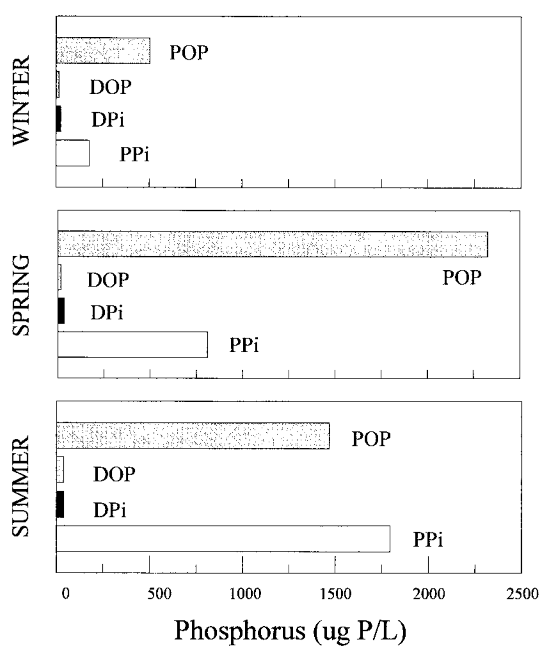

Figure 9. Seasonal comparisons of mean phosphorus concentrations in storm discharges from the cropland watershed (109). Abbreviations of P forms are as in Figure 5.

3.5. Nitrogen to Phosphorus Ratios

Atomic ratios of total N (TN/TP) and total P (TIN/TIP) declined significantly with intensity of storm discharge from the mixed-land-use watershed (Figure 11). TN/TP ratios were above 15 in low-intensity storms but declined to less than five during intense storm events. For TIN/TIP ratios the decline was larger, from around 30 for low-intensity storms to about two in high-intensity storms. When storm events were examined on a seasonal basis, the same patterns were found, with only minor seasonal differences. For the cropland watershed, similar relationships between TN/TP atomic ratios were found, and a power function regression was significant ($R^2 = 0.52$ and $P < 0.01$), but the relationship for TIN/TIP atomic ratios was not as strong ($R^2 = 0.26$ and $P = 0.09$). There was little or no relationship between peak water discharge during storms and the ratio of POP/TPi, POP/PPi, PON/POP, or PON/TIN, either seasonally or annually for any of the watersheds.

3.6. Comparison of Storms and Base Flows

Nutrient concentrations in individual samples taken during storm events were compared with concentrations during base flows prior to and subsequent to the storm events (Table 3). Nitrate concentrations were significantly higher in storm samples than in base flow for the mixed-land-use watershed (101) and the forested watershed (110). Ammonium concentrations were significantly higher in storm samples than in base flow from the grazed watershed (111). Total organic N, total phosphate, and total organic P concentrations were significantly higher in storm samples than in base flow from all watersheds.

4. Discussion

This study was unique in that it examined the relationships between peak water discharge over a broad range of storm

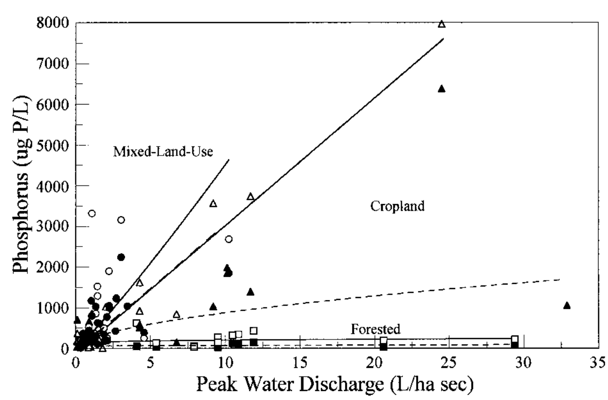

Figure 10. Variations in volume-integrated mean phosphorus concentrations for a given storm with peak water discharge for that storm. Solid lines and open data points are for POP; dashed lines and solid data points are for PPi concentrations. Round, triangular, and square data points are for the mixed (101), cropland (109), and forested (110) watersheds, respectively.

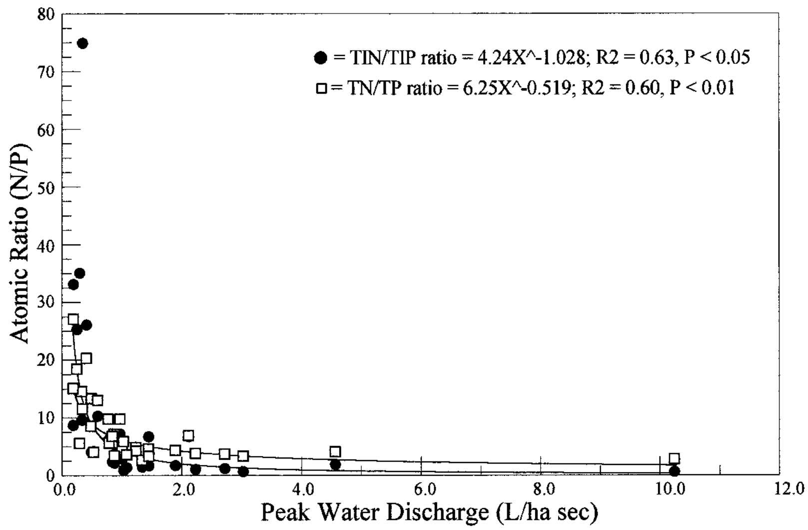

Figure 11. Variations in volume-integrated mean atomic ratios of N/P for a given storm with peak water discharge for that storm from the mixed-land-use watershed (101). Solid circles are data for total inorganic N to total inorganic P ratios; open squares are data for total N/total P ratios.

intensities and concentrations of dissolved and particulate N and P species on four closely situated watersheds with differing land use. Although one might be concerned at the lack of replication of land uses in this study, the effects of these land uses on Rhode River watershed seasonal and annual N and P fluxes have been documented previously from these and other nearby subwatersheds [*Correll and Dixon*, 1980; *Correll et al.*, 1992].

We found that it was the concentration of particulate nutrients (POP, PPi, and PON) which were responsible for most of the increases in total N and P during storm events. What was the origin and composition of these particulates? Since the particulates are transported in overland flows during storms, these particulate nutrients are probably derived from surface soils and organic litter on the soil surface. One might assume that the POP came from detritus rather than surface soil, but of the total P in surface soils, 70% and 25% is organic P on the forested and cropland watersheds, respectively [*Vaithiyanathan and Correll*, 1992]. Since the proportions of POP found in these storms was higher than these soil composition values, it seems likely that the POP was a combination of soil organic P and surface detritus. The PPi was probably composed primarily of iron phosphates (both occluded and nonoccluded), since the inorganic phosphate in the surface soils on these watersheds is dominated by iron phosphate and there are almost no calcium or aluminum phosphates [*Vaithiyanathan and Correll*, 1992]. Phosphate sorption to the particulate iron in these soils is reversible when suspended in water [*Correll*, 1998; *Froehlich*, 1988]. The nonoccluded iron phosphate can quickly reequilibrate with dissolved phosphate, while the occluded iron phosphate reequilibration is much slower.

Although storm events are known to be important periods for the transport of some forms of nitrogen and phosphorus, especially particulate forms, and although there are many reports on nutrient exports from various watersheds, there is a dearth of literature on the effects of land use and storm intensity on nutrient concentrations in watershed storm discharges. This study adds significantly to the knowledge base on this topic.

A paired, small watershed study of pasture, pine plantation, and native podocarp forest in New Zealand [*Cooper and Thomsen*, 1988] reported the results of a fairly large number of spot samplings for DPi, TP, TKN, dissolved Kjeldahl N, DNH4, and nitrate. Only the means and ranges of concentrations segregated into times of base flow and storm flow were reported. Their results indicate that nutrient concentrations were higher during storm events, especially for nutrients composed predominantly of particulate forms and that nutrient concentrations were different among land use categories. During storms, mean concentrations of all nutrient fractions except nitrate were higher for the pasture watershed and were lowest for the pine plantation watershed. Nitrate concentrations during storms were higher for the native podocarp watershed.

Several studies found that nitrate concentrations declined or remained about the same during storm events [*Burt and Arkell*, 1987; *Correll et al.*, 1987; *O'Brien et al.*, 1993], while another study tracked the changes in nitrate and DPi concentrations during one hydrograph [*McDiffett et al.*, 1989]. These reports agreed that the concentrations of these dissolved inorganic forms of nutrients remained low and did not change a great deal during storm events.

Two reports examined the changing concentrations of DPi and various fractions of particulate P during the course of several storms on two watersheds [*Kunishi et al.*, 1972; *Pionke and Kunishi*, 1992]. These studies focused on whether particulate phosphate was available for exchange with dissolved phosphate or was biologically available. They concluded that about half of the PPi was exchangeable or readily bioavailable and that most of the total P was discharged during storms as particulate P. Another study focused on phosphorus sorption and availability for losses in runoff as surface soils become P saturated in the Atlantic Coastal Plain [*Mozaffari and Sims*, 1994]. As these soils approach P saturation, they provide the potential for greatly increased losses of dissolved forms of phosphorus to local streams. While this P saturation condition is not present on Rhode River watershed, at locations where P saturation or near saturation occurs one would expect to have different phosphorus behavior during storm events.

None of these studies directly addressed the central focus of this report, which is the effects of land use and storm intensity on the discharge of particulate and dissolved forms of nitrogen and phosphorus. Are these results from the Rhode River typical of the mid-Atlantic Coastal Plain? The forested watershed (110) was completely vegetated with deciduous hardwood forest, mostly old growth, and had very little human disturbance in the last 50 years other than atmospheric deposition [*Vaithiyanathan and Correll*, 1992]. Thus it provided a good measure of how effectively natural vegetation in this region can retain nutrients during storms. The cropland watershed (109) was in continuous corn production and had no winter cover crops. Corn is the most extensive row crop in this region. A continuous forest riparian buffer occupied 36% of the watershed and has been shown to remove most of the nitrate entering it from the croplands in overland storm flows and groundwater during all seasons [*Peterjohn and Correll*, 1984; *Correll and Weller*, 1989]. The buffer has also been shown to remove significant amounts of particulate P and N from overland storm flows [*Peterjohn and Correll*, 1984]. The mixed-land-use watershed (101) also had essentially continuous riparian forest buffers. Without these riparian forest buffers, nutrient fluxes would probably have been higher. The grazed watershed (111) was rotationally grazed by cattle with little or no import of exogenous nutrients from outside the watershed as fertilizer or cattle food supplements. It was therefore a low-intensity pasture system.

Some data are available from 10 watersheds on the eastern shore of Chesapeake Bay, which can be compared with data from this study on the western shore [*Jordan et al*., 1997a]. For watersheds with similar land use, Rhode River watersheds seemed to discharge higher concentrations of total organic nitrogen (TON) for the same time period. Discharges of suspended particulates were higher for Rhode River watersheds, but the suspended material had about the same content of total organic P (TOP) and total inorganic P (TPi). Erosion rates are unusually high on Rhode River watersheds because of the steep slopes and highly erodible soils characteristic of the inner Coastal Plain. Therefore the yield of particulate nutrients from Rhode River watersheds in storms is higher than found in some areas of the Coastal Plain.

Our results are consistent with known land use effects on the concentrations of nitrogen (Figure 4) and phosphorus (Figure 5) discharged during storms. Not only were the concentrations different, but the proportions of the various forms of nutrient differed among watersheds. The higher proportion of total organic P we found in forest discharges (77%, Figure 5) rather than in cropland discharges (64%, Figure 5) and the lower proportion of total inorganic P we found in forest discharges rather than in cropland discharges (23 versus 36%, Figure 5) probably relate to differences in surface soil composition [*Vaithiyanathan and Correll*, 1992]. Forest surface soils had about twice as much organic P and only about 29% as much inorganic P as cropland [*Vaithiyanathan and Correll*, 1992]. We also found evidence of seasonality in the proportions of nitrogen (Figures 6 and 7) and phosphorus (Figures 8 and 9) discharged from a mixed-land-use watershed and a cropland watershed. Some of this seasonality was probably related to the fact that in this region the most intense storms occur in the summer and the storms are less intense in the winter. The low mean ratio of DNH4/PNH4 in storm discharges from the forested watershed (0.75, Figure 4) may be related to the quality of the particulate matter in the discharges. This ratio was 1.6, 1.9, and 4.3 for the grazed, mixed-land-use, and cropland watersheds, respectively.

One expects to see higher nutrient fluxes during storm events because of the higher rates of water discharge. We found, however, that concentrations of some types of nutrient also increased dramatically during storm events. Peak water discharge was correlated with mean particulate nutrient concentrations in storm discharges. Therefore one would expect that the more intense summer storms would have a higher proportion of particulate nutrients than the winter storms, which is what we found (Figures 6–9). The strong correlation of particulate nutrient concentrations with peak water discharge rates makes it much easier to predict storm discharges of nutrients. This relationship eliminates the need to know rainfall volumes and intensities, since peak water discharge is a measurement much more directly related to nutrient discharge. One should note, however, that the smaller, first-order watersheds were observed to have shorter, more intense storm discharges than the larger second-order watershed (Table 2). Thus the mean and maximum observed peak water discharge rates were much higher. The regression slopes for POP and PPi concentration versus peak water discharge were higher for the mixed-land-use watershed than even the cropland watershed (Figure 10).

Ammonium concentrations also increased significantly with peak water discharge, but the slopes were much lower than for PON. Other than ammonium, dissolved forms of N and P did not increase significantly with peak water discharge. Therefore some ratios of forms of nitrogen to forms of phosphorus changed with peak water discharge (e.g., Figure 11). TN/TP ratios declined about fourfold because in storm events particulate P concentrations increased dramatically and most of the phosphorus discharged was particulate (Figures 5, 8, and 9); while for total N, although PON increased, substantial percentages were always in dissolved forms, which did not increase significantly. TIN/TIP ratios declined about tenfold to fifteenfold because most of the inorganic P was in the form of PPi (Figures 5, 8, and 9), which increased substantially with discharge intensity, while most of the inorganic N was in the form of nitrate (Figures 4, 6, and 7), which did not increase significantly with peak water discharge.

How significant are these storm events to the receiving waters in Chesapeake Bay? Eutrophication is a serious problem in Chesapeake Bay and in many of its subestuaries, such as the Rhode River. This eutrophication is believed to be caused by excessive inputs of nitrogen and phosphorus [*Correll*, 1987; *Fisher et al*., 1992], although light sometimes becomes limiting in conditions of excessive nutrient inputs [*Gallegos et al*., 1997]. Most of the phosphorus in the storm discharges was particulate. Only DPi is available for assimilation by phytoplankton and other microbiota [*Correll*, 1998]. However, much of the PPi in storm discharges is in equilibrium with DPi [*Froehlich*, 1988], and the majority of the POP is gradually mineralized to PPi and DPi by diagenesis (microbial activity) in the estuarine bottom sediments [*Boynton and Kemp*, 1985; *Jordan et al*., 1991]. The release of DPi from estuarine bottom sediments is more efficient in estuaries than in freshwater systems, primarily because of anaerobic conditions and the presence of high sulphate concentrations [*Correll*, 1998]. The proportion of PON that is released as DNH_4 is not as well understood, and the proportion may be smaller. Since both TN/TP and TIN/TIP ratios declined to well below the Redfield ratio of 16 [*Redfield*, 1958], large storm events may bring about temporary nitrogen limitations in receiving waters. If storm events are not adequately sampled, serious underestimates of phosphorus flux and overestimates of nitrogen to phosphorus ratios will result. For example, one large summer storm (Figures 2 and 3) delivered 24% of the total P, 18% of the TPi, 30% of the TOP, and 18.5% of the TON flux for the entire summer. Likewise, one large spring storm on the mixed-land-use watershed delivered 39% of the total P, 41% of the TPi, 38% of the TOP, and 12% of the TON for the entire spring in a year with normal spring precipitation.

Acknowledgments. This research was supported by a series of grants from the Smithsonian Environmental Research Program, the National Science Foundation, the Environmental Protection Agency, and the National Oceanic and Atmospheric Agency's Coastal Oceans Program.

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(Received June 3, 1998; revised February 22, 1999;
accepted March 2, 1999.)