Estuaries Vol. 26, No. 2A, p. 226–243 April 2003

Sources of Nutrient Inputs to the Patuxent River Estuary

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ABSTRACT: We quantified annual nutrient inputs to the Patuxent River estuary from point and nonpoint sources and from direct atmospheric deposition. We also compared nonpoint source (NPS) discharges from Piedmont and Coastal Plain regions and from agricultural and developed lands. Using continuous automated-sampling, we measured discharges of water, nitrogen, phosphorus, organic carbon (C), and suspended solids from a total of 23 watersheds selected to represent various proportions of developed land and cropland in the Patuxent River basin and the neighboring Rhode River basin. The sampling period spanned two years that differed in annual precipitation by a factor of 1.7. Water discharge from the watershed to the Patuxent River estuary was 3.4 times higher in the wet year than in the dry year. Annual water discharges from the study watersheds increased as the proportion of developed land increased. As the proportion of cropland increased, there were increases in the annual flow-weighted mean concentrations of nitrate (NO_3^-), total nitrogen (TN), dissolved silicate (Si), total phosphate (TPO_4^{3-}), total organic phosphorus (TOP), total P (TP), and total suspended solids (TSS) in NPS discharges. The effect of cropland on the concentrations of NO_3^- and TN was stronger for Piedmont watersheds than for Coastal Plain watersheds. As the proportion of developed land increased, there were increases in annual mean concentrations of NO_3^-, total ammonium (TNH_4^+), total organic N (TON), TN, total organic C (TOC), TPO_4^{3-}, TOP, TP, and TSS and decreases in concentrations of Si. Annual mean concentrations of TON, TOC, forms of P, and TSS were highest in the wet year. Annual mean concentrations of NO_3^-, TNH_4^+, TN, and Si did not differ significantly between years. We directly measured NPS discharges from about half of the Patuxent River basin and estimated discharges from the other half of the basin using statistical models that related annual water flow and material concentrations to land cover and physiographic province. We compared NPS discharges to public data on point source (PS) discharges. We estimated direct atmospheric deposition of forms of N, P, and organic C to the Patuxent River estuary based on analysis of bulk deposition near the Rhode River. During the wet year, most of the total terrestrial and atmospheric inputs of forms of N and P came from NPS discharges. During the dry year, 53% of the TNH_4^+ input was from atmospheric deposition and 58% of the NO_3^- input was from PS discharges; NPS and PS discharges were about equally important in the total inputs of TN and TPO_4^{3-}. During the entire 2-yr period, the Coastal Plain portion of the Patuxent basin delivered about 80% of the NPS water discharges to the estuary and delivered similar proportions of the NPS TNH_4^+, TN, TOP, and TSS. The Coastal Plain delivered greater proportions of the NPS TON, TOC, Si, and TP (89%, 90%, 93%, and 95%, respectively) than of water, and supplied nearly all of the NPS TPO_4^{3-} (99%). The Piedmont delivered 33% of the NPS NO_3^- while delivering only 20% of the NPS water to the estuary. We used statistical models to infer the percentages of NPS discharges supplied by croplands, developed lands, and other lands. Although cropland covers only 10% of the Patuxent River basin, it was the most important source of most materials in NPS discharge, supplying about 84% of the total NPS discharge of NO_3^-; about three quarters of the TPO_4^{3-}, TOP, TP, and TSS; and about half of the TNH_4^+ and TN. Compared to developed land, cropland supplied a significantly higher percentage of the NPS discharges of NO_3^-, TN, TPO_4^{3-}, TOP, TP, and TSS, despite the fact developed land covered 12% of the basin.

Introduction

Increased loadings of nitrogen (N), phosphorus (P), and organic carbon (C) from fertilizer, sewage, erosion, and atmospheric pollution have contributed to eutrophication of estuarine and coastal waters around the world (Nixon 1995; Carpenter et al. 1998; Conley 2000; Cloern 2001). In Chesapeake Bay, one of the world's largest estuaries, anthropogenic increases in inputs of both N and P have led to excessive plankton production (Boynton et al. 1982; Malone et al. 1986, 1988; Correll 1987; Harding 1994), which has contributed to the demise of submerged aquatic vegetation (Kemp et al. 1983; Orth and Moore 1983) and the increase in the extent of hypoxic waters (Taft et al. 1980; Officer et al. 1984). Elevated N and P inputs have also led to seasonal depletion of dissolved silicate (Si), resulting in altered phytoplankton production and species composition in the middle to lower Bay (D'Elia et al. 1983; Anderson 1986; Conley and Malone 1992). Similar effects of eutrophication have been documented in the Patuxent River estuary (Boynton et al. 1995; D'Elia et al. 2003; Stankelis et al. 2003), a tributary estuary of Chesapeake Bay and the subject of this study.

Efforts to control eutrophication require an understanding of the sources of nutrient loading to

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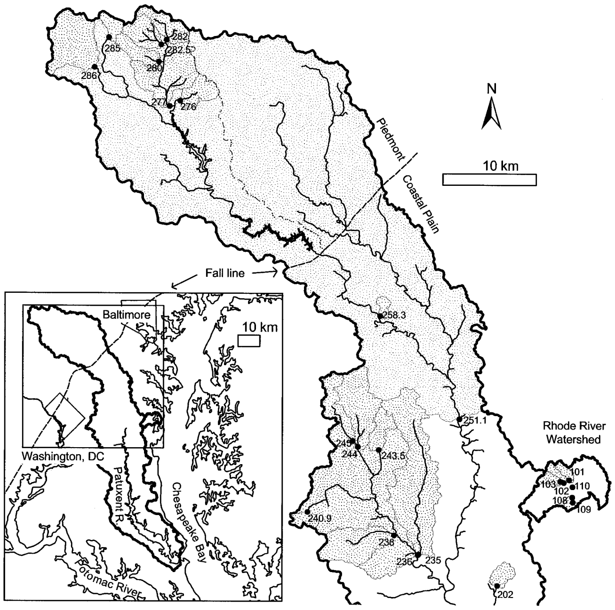

Fig. 1. Study watersheds (shaded) in the Patuxent and Rhode River basins. Sampling points are labeled with watershed numbers. Inset shows entire Patuxent River basin in relation to nearby cities and Chesapeake Bay. The fall line is the boundary between the Piedmont (north of the line) and the Coastal Plain. A dotted and dashed line separates the Piedmont into a western portion draining into reservoirs and an eastern portion without reservoirs.

estuaries. Several studies have shown that nonpoint source (NPS) discharges of nutrients from watersheds are enhanced by agricultural (e.g., Reckolainen 1990; Jordan et al. 1997a,b) and urban or suburban (e.g., Frink 1991; Short and Burdick 1996) land uses. Hydrologic (e.g., Jordan et al. 1997c) and geologic (e.g., Grobler and Silberbauer 1985) differences among watersheds can interact with land use to alter nutrient discharges.

The temporal variability of water flow makes it difficult to quantify NPS discharges to estuaries. Brief periods of high flow following heavy precipitation can carry much of the annual discharges of particulate matter and P (Kronvang 1992). Interannual variability of watershed discharges (e.g., Correll et al. 1999a,b,c) can obscure long-term trends in nutrient loading linked to changes in land use. There remains much uncertainty in estimating current and future NPS discharges. Because of the uncertainties about nutrient inputs from land, few studies have linked the dynamics of changing nutrient inputs with ecological responses in estuaries (e.g., Jordan et al. 1991a,b; Gallegos et al. 1992).

The Patuxent River estuary can serve as a model system for examining sources of nutrient inputs from the watershed and the ecological responses to those inputs in the estuary. Several decades of research have documented the effects of human impacts on the watershed and the estuary (e.g., Boynton et al. 1995; D'Elia et al. 2003). The present study is a component of a larger National Oceanic and Atmospheric Administration-funded study that investigates the effects of multiple stressors in the Patuxent estuary and the role of ecological complexity in modifying those effects (COmplexity And STressors in Estuarine Systems, COASTES, Breitburg et al. 1999, 2003). Here we examine the rates, controls, and pathways of delivery of nutrients, organic C, and sediments to the Patuxent River estuary. Other components of the COASTES project predict future changes in terrestrial inputs (Weller et al. 2003), how changing inputs will alter water quality within the estuary (Lung and Bai 2003), and how estuarine biota will respond (e.g., Breitburg et al. 2003; Weigner et al. 2003).

The objectives of this paper are to quantify the annual nutrient inputs to the Patuxent River estuary from point sources (PS) and NPS, and direct atmospheric deposition; and to compare NPS releases from different physiographic regions and from agricultural and developed lands. During 2 yrs with contrasting water flow, we measured discharges of water, nutrients, organic C, and suspended solids from several watersheds in or adjacent to the Patuxent River basin. As in similar previous studies (Jordan et al. 1997a,b), the watersheds were selected to represent various land cover compositions. Unlike our previous studies, this study examined effects of developed or urbanized land as well as the effects of agricultural land. We used linear statistical models to infer the separate effects of developed land and cropland, and to predict NPS discharges from unmonitored parts of the basin. To complete our analysis of terrestrial and atmospheric inputs to the estuary, we also measured atmospheric deposition of N, P, and C forms, and we used publicly available data to account for PS inputs.

Study Watersheds

We developed geographic descriptions of the study watersheds using Arc/Info geographic information system software to digitize watershed boundaries (Weller et al. 2003). Existing digital maps provided data on land cover from 1988–1991 (Environmental Protection Agency-Environmental Monitoring and Assessment Program [EPA-EMAP] 1994) and on the location of the boundary between the Coastal Plain and Piedmont physiographic provinces (Langland et al. 1995). The 2,290-km^2 Patuxent River basin includes land from the Piedmont and Coastal Plain physiographic provinces in Maryland, U.S. (Fig. 1, Table 1).

TABLE 1. Total areas (km^2) and percentages of land cover types (EPA-EMAP 1994) in study watersheds and major subbasins of the Patuxent River Basin. Watersheds 101–110 are in the Rhode River basin. Watersheds 202–258.3 are in the Coastal Plain in the Patuxent River basin. Watersheds 276–286 are in the Piedmont in the Patuxent River basin. Watershed 251.1 includes Coastal Plain and Piedmont lands. Major subbasins of the Patuxent include Piedmont draining to reservoirs or not draining to reservoirs, whole Piedmont, Coastal Plain in watershed 251.1, unmonitored Coastal Plain, and whole Coastal Plain.

Watershed	Land Area	Forest	Grassland	Developed	Cropland
101	2.3	52	33	4.8	10
102	1.9	56	29	5.7	8.5
103	2.5	71	23	2.0	4.4
108	1.5	51	28	6.6	15
109	0.17	40	45	0	15
110	0.062	100	0	0	0
202	4.8	28	41	1.1	31
235	230	37	33	23	6.9
236	61	44	26	16	14
238	23	33	44	11	12
240.9	4.0	3.5	26	70	0
243.5	7.3	29	48	16	6.8
244	24	34	22	44	0
245	15	25	12	63	0
251.1	900	44	29	19	7.8
258.3	2.1	95	1.6	3.1	0.47
276	9.1	31	51	3.3	15
277	58	35	47	1.6	17
280	7.9	38	42	0	20
282	10	23	54	0.087	23
282.5	11	28	49	5.8	17
285	4.5	23	57	0	21
286	28	51	35	2.6	12
Piedmont with reservoirs	340	46	39	4.2	11
Piedmont with no reservoirs	290	36	33	23	7.9
Coastal Plain in 251.1	270	49	13	34	3.9
Unmonitored coastal plain	1,100	56	26	4.1	12
Whole Piedmont	630	42	36	13	9.5
Whole Coastal Plain	1,600	52	25	12	10
Whole Patuxent Basin	2,300	49	28	12	10

About 27% of the basin is in the Piedmont. About half of this Piedmont portion drains into two reservoirs from which much of the water is withdrawn for use outside of the basin. The entire Patuxent River basin is 49% forest, 28% grassland, 12% developed land, and 10% cropland (Table 1). We monitored discharges of water, nutrients, sediments, and organic C from 7 watersheds in the Piedmont and 15 watersheds in the Coastal Plain (Fig. 1). The watersheds included various proportions of cropland and developed land and no significant PS (Table 1). Most of the study watersheds are in the Patuxent River basin, but 6 of the Coastal Plain watersheds are in the adjacent Rhode River basin and have been monitored since the early 1970s (e.g., Correll et al. 1999a,b,c). We also monitored discharges from the 901-km^2 watershed of the mainstem of the Patuxent River just upstream of the tidal freshwater portion of the estuary near Bowie, Maryland (watershed 251.1; Fig. 1, Table 1). This watershed includes all of the Piedmont portion and some of the Coastal Plain portion of the Patuxent river basin as well as 7 of the 8 of major PS in the basin. Monitoring discharges from the mainstem watershed (251.1) provided a direct measurement of terrestrial inputs from 40% of the Patuxent basin. Monitoring watersheds 235 and 202 (Table 1) provided coverage of another 10% of the basin so that altogether discharges from about half of the basin were directly measured.

Materials and Methods

Flow Measurements and Sampling

We used automated samplers to monitor discharge of water and collect water samples from the streams that drain the study watersheds. Automation ensures adequate sampling of particulate fractions in storm flow (e.g., Jordan et al. 1986). 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 versus depth (Jordan et al. 1997a).

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 (Chow 1964). For each stream, 6–15 measurements of flow rate were made during a range of high and low flow conditions throughout the study. The rating curve equations were derived from regressions of the logarithm of flow rate against the logarithm of depth.

The automated samplers 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 (Jordan et al. 1997a,b). Samples were pumped more frequently at higher flow rates, up to once every 5 min during storm flow. Samples were pumped through plastic tubing that was first rinsed with stream water. Two sets of flow-weighted composite samples, one with sulfuric acid as a preservative, were collected 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 well-mixed throughout their cross sections.

The sampling reported here covered a 2-yr period from July 29, 1997, through August 2, 1999. 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 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.

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 preservative to these grab samples because the acid preservative dissolves some of the particulate nutrients. 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.

As part of our long-term program of precipitation monitoring at the Rhode River watershed, we sampled bulk precipitation for chemical analysis using a funnel set on top of a tower extending above the surrounding tree canopy (e.g., Correll et al. 1994; Jordan et al. 1995). Precipitation volume was measured with standard rain gauges at the Rhode River watershed and at the sampling stations for watersheds 235, 236, 280, and 285.

CHEMICAL ANALYSES

We used the following techniques for analysis of N, P, and organic C species in the acid-preserved samples and in bulk precipitation samples. Total P was digested to phosphate (PO_4^{3-}) with perchloric acid (King 1932). PO_4^{3-} in the digestate and in undigested aliquots was analyzed by reaction with stannous chloride and ammonium molybdate (American Public Health Association [APHA] 1995). The PO_4^{3-} in the undigested, acid-preserved samples is total phosphate (TPO_4^{3-}), the sum of dissolved plus acid-extractable particulate PO_4^{3-}. The concentration of TPO_4^{3-} 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 1995). NH_4^+ in undigested aliquots was analyzed by oxidation to nitrite with alkaline hypochlorite (Strickland and Parsons 1972) and analysis of the nitrite by reaction with sulfanilamide (APHA 1995). The NH_4^+ in the acid-preserved samples is total ammonium (TNH_4^+), the sum of dissolved plus acid-extractable particulate NH_4^+. Total organic N (TON) was calculated by subtracting TNH_4^+ from total Kjeldahl N. For watershed samples, 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 1995). For bulk precipitation samples, NO_3^- was measured directly using a Dionex ion chromatograph. Total organic C (TOC) was analyzed as chemical oxygen demand by drying samples at 60°C, followed by reaction with potassium dichromate in 67% sulfuric acid at 100°C for 3 h (Maciolek 1962; APHA 1995). Organic C was calculated from the amount of unreacted dichromate measured colorimetrically (Maciolek 1962; Gaudy and Ramanathan 1964).

We measured concentrations of total suspended solids (TSS) and dissolved Si in the unpreserved composite samples. TSS 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

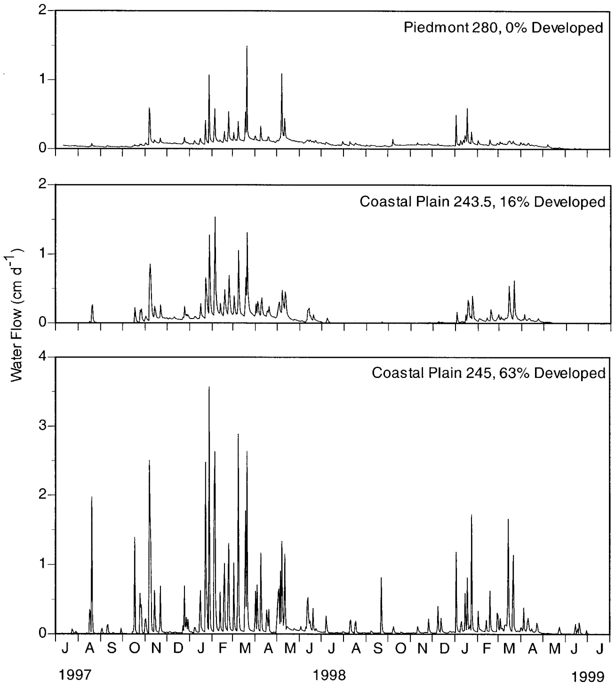

Fig. 2. Daily water flow (cm d^{-1}) from three watersheds during the two-year study.

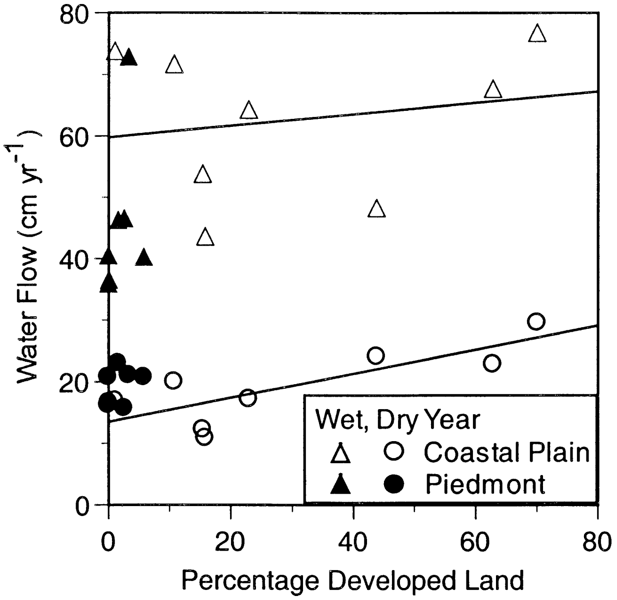

Fig. 3. Annual water flow (cm yr^{-1}, 1 cm = 100 m^3 ha^{-1}) versus percentage of developed land for study watersheds that are > 4 km^2 and < 250 km^2. Triangles represent data from the wet year; circles represent dry year. Filled symbols represent Piedmont watersheds; open symbols represent Coastal Plain watersheds. Lines are fit by linear regression. Upper line is fit to Coastal Plain data from the wet year. Lower line is fit to Coastal Plain data from the dry year.

the filter after drying it in a vacuum desiccator. Si was analyzed in 0.45-µm filtered samples by automated colorimetry (Technicon method 696-82W).

Results

WATER DISCHARGE

Water flow varied with weather, season, and year. The magnitude of variability in daily flow was influenced by province and by the percentage of developed land. Water flow from Piedmont watersheds was steadier and more dominated by base flow than was flow from Coastal Plain watersheds (Fig. 2), as we have previously documented (Jordan et al. 1997c). Flow also increased in variability and reached higher peak rates per watershed area as the percentage of developed land increased. This is probably due to increased runoff from impervious surfaces such as pavement and roofs. Superimposed on daily variations associated with runoff events are the typical seasonal changes, with greater discharges in winter and spring than in summer and fall because of the seasonal changes in evapotranspiration (Fig. 2).

Annual water discharges were about three times higher during the first year of the study than during the second year due to differences in precipitation (Fig. 3). The first year of the study was unusually wet, with precipitation at Coastal Plain and Piedmont sites averaging 125 and 118 cm, respectively. The second year was a drought with precipitation at Coastal Plain and Piedmont sites averaging only 72 and 70 cm, respectively. By comparison, the regional 160-yr mean annual precipitation is 108 cm with a standard deviation of 21.8 cm (Correll et al. 1999a). The differences in water discharges between the two years were even greater than the differences in precipitation (Fig. 3), suggesting that evapotranspiration did not differ as much between years.

Annual water discharge also differed with land cover, increasing with higher proportions of developed land (Fig. 3), probably due to increased runoff from impervious surfaces. Annual water discharge per area was lowest for Coastal Plain watersheds smaller than 4 km^2, which included the Rhode River watersheds and watershed 258.3 (Table 1). This previously observed effect of size (Jordan et al. 1997a) could mask effects of land cover. We omitted watersheds smaller than 4 km^2 from statistical analyses of the effects of year, province, and land cover on water flow. We also omitted the largest watershed (251.1) because it includes PS, reservoirs, and both Piedmont and Coastal Plain lands. The linear statistical analysis of the annual water discharges showed highly significant effects ($p < 0.01$) of year and percentage of developed land (Table 2). The effects of year alone explained 73% of the variance among annual discharges,

TABLE 2. Percentages of variance explained by linear statistical models that relate NPS water flow to different factors. Models were fit with the GLM procedure of the Statistical Analysis System (SAS Institute, Inc. 1999). Each percentage of variance explained is for a model including the factor on the line and all factors on previous lines. Asterisks indicate significance of the factor on the line: ** $0.05 > p > 0.01$, *** $p < 0.01$.

Factor	% Variance Explained
Year	73***
% Developed Land	78***
% Cropland	79
Province	80
Year × % Developed	81
Year × % Cropland	81
Year × Province	85**
% Cropland × Province	87**

while a model including just the effects of year and percentage of developed land explained 78% of the variance. There were no significant main effects of province or percentage of cropland, but the interactions of province with year and with percentage of cropland were significant. Interaction between developed land and province was not tested because our study watersheds in the Piedmont did not represent a sufficient range of percentage of developed land. Our full model explained 87% of the variance among annual water discharges (Table 2). The interaction of province and year is probably due to the difference in rainfall between the provinces during the wet year.

We calculated annual water flows to the entire Patuxent estuary based on our measurements of precipitation and watershed discharges and on public information about wastewater discharges and withdrawals and releases of water from the reservoirs. We estimated NPS water discharges from the unmonitored Coastal Plain area (Fig. 1) using a statistical model, which included these significant factors (Table 2): year, the percentage of developed land, and the interaction of province with year. The nonsignificant factor province was also included due to including the significant interaction of province with year. We excluded the marginally significant interaction of province with cropland ($p = 0.043$) because otherwise the model projected unrealistic water flow from watersheds with low proportions of cropland. The simplified model explained 83% of the variance in water flow. According to the model, annual NPS water flow ($m^3\ ha^{-1}$) from the Coastal Plain was 15.12 times the percentage of developed land plus either 5,782 $m^3\ ha^{-1}$ in the wet year, or 1,460 $m^3\ ha^{-1}$ in the dry year. We estimated NPS water discharge from the largest monitored portion of the watershed (watershed 251.1; Fig. 1, Table 1) by subtracting the wastewater discharges from the total measured discharge. Measured discharges of the Western Branch drainage in the Coastal Plain (study watershed 235) represented NPS water discharge for 10% of the Patuxent basin.

TABLE 3. Annual freshwater flows ($10^6\ m^3$) including: NPS discharge to streams from monitored and unmonitored watersheds, withdrawal from reservoirs, net gain of water stored in reservoirs (negative gain = net loss), NPS and PS discharges delivered to the estuary, and direct atmospheric deposition onto the estuary during the two years of the study.

Sources	Water Flow	
	Wet Year	Dry Year
NPS to Streams		
Monitored	602	220
Unmonitored	663*	172*
Total	1,265	392
Removal in Reservoirs		
Withdrawal	85	65
Net Storage Gain	3.4	−18
Total	88.4	47
Flows to Estuary		
NPS	1,177	345
PS	73	69
Atmospheric	171	99
Total	1,422	512

* Modeled with 95% confidence limits ± 97 ($10^6\ m^3$).

NPS discharge was the largest component of the total water inflow to the Patuxent estuary but it differed between years more than did water flows from other sources (Table 3). NPS flow was 3.4 times higher in the wet year than in the dry year, while direct precipitation onto the estuarine surface was only 1.7 times higher in the wet year than in the dry year and wastewater discharge was about the same in both years. The NPS flow was proportionately greater in the wet year, supplying 83% of the total water influx in the wet year but only 67% in the dry year (Table 3). About half of the total NPS flow came from the unmonitored Coastal Plain area. Estimating the unmonitored flow using our statistical model introduced some uncertainty. The 95% confidence interval for the predicted flow from the unmonitored area was about 8% of the total NPS flow reaching the estuary in the wet year and about 28% in the dry year (Table 3). Some of the water discharged by the Piedmont portion of the Patuxent River basin was diverted through a reservoir system to public use outside of the basin. This water withdrawal was about equal to discharge of wastewater within the entire basin (Table 3).

MATERIAL CONCENTRATIONS IN NPS DISCHARGES

While water flow was most strongly influenced by year, the annual flow-weighted mean concentrations of most materials were more strongly influ-

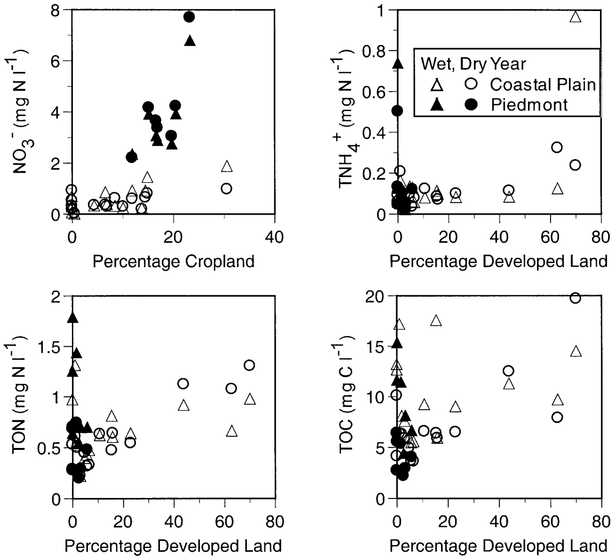

Fig. 4. Annual flow-weighted mean concentrations of NO_3^-, TNH_4^+, TON, and TOC (mg N or C l^{-1}) versus percentage of cropland or versus percentage of developed land. Triangles represent data from the wet year; circles represent dry year. Filled symbols represent Piedmont watersheds; open symbols represent Coastal Plain watersheds.

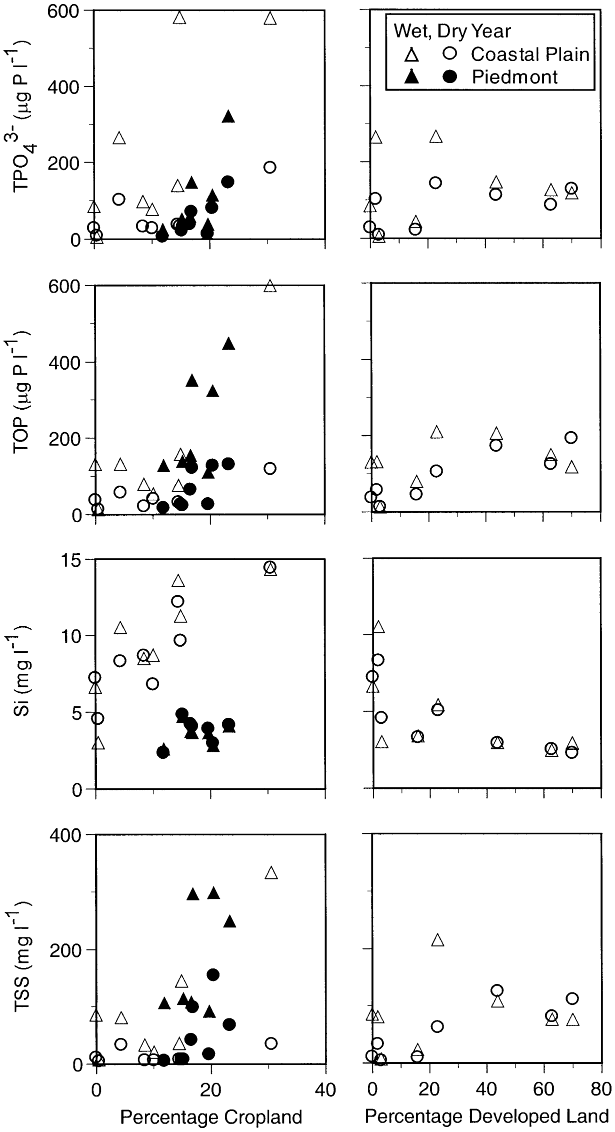

Fig. 5. Annual flow-weighted mean concentrations of TPO_4^{3-} (μg P l^{-1}), TOP (μg P l^{-1}), Si (mg l^{-1}), and TSS (mg l^{-1}) versus percentage of cropland and versus percentage of developed land. Because the concentrations are affected both by the percentages of cropland and developed land, data for watersheds with < 7% developed land are plotted versus percentage of cropland and data for watersheds with < 7% cropland are plotted versus percentage of developed land. Triangles represent data from the wet year; circles represent dry year. Filled symbols represent Piedmont watersheds; open symbols represent Coastal Plain watersheds.

enced by geographic factors, such as land cover and province (Figs. 4 and 5). We investigated these effects with linear statistical models that first accounted for the main effects and interactions of geographic factors and then for the main effects and interactions of year (Table 4). The full models explained 50–89% of the variance in concentrations (Table 4). Concentrations of NO_3^-, TNH_4^+, total nitrogen (TN), and Si varied significantly with geographic factors but did not differ significantly between years. In contrast, concentrations of TON, TOC, TSS, and all forms of P showed significant effects of year as well as effects of geographic factors. Land cover affected the concentrations of all materials. The relative importance of cropland versus developed land differed among materials and differed according to the order in which the factors were entered into the models. Models with cropland factors entered first were compared to models with developed land factors entered first (Table 4). Either sequence of factors may be valid because there are no a priori reasons to assign priority to cropland versus developed land factors. NO_3^- concentrations increased as the percentage of cropland increased; and this effect was much stronger in the Piedmont than in the Coastal Plain (Fig. 4). Si concentrations increased with the percentage of cropland and decreased with the percentage of developed land (Fig. 5). Concentrations of TSS and materials that include high proportions of particulate forms (Figs. 4 and 5) were generally higher in the wet year than in the dry year. When the effect of land cover was significant (Table 4), there was an increase in concentration with increasing cropland or developed land (Figs. 4 and 5), except for the decrease in Si concentration with increasing developed land (Fig. 5).

The variance of TNH_4^+ concentration was the

TABLE 4. Percentages of variance explained by linear statistical models that relate NPS concentrations to different factors. Two model structures are shown: one with cropland factors entered first and one with developed land factors entered first. The models were fit with GLM (SAS Institute, Inc. 1999). Each percentage of variance explained is for a model including the factor on the line and all factors on previous lines. Asterisks indicate type I significance of the factor on the line: * $0.1 > p > 0.05$, ** $0.05 > p > 0.01$, *** $p < 0.01$.

Factor	NO_3^-	TNH_4^+	TNH_4^{+a}	TON	TN	TOC	Si	TPO_4^{3-}	TOP	TP	TSS
Cropland 1st											
% Cropland	42***	0.4	0.5	3	37***	1	12***	8***	13***	12***	11***
% Developed Land	42	28***	48***	28***	40***	20***	17***	13*	24***	20***	18**
Province	80***	29	50	29	73***	23	75***	35***	25	30***	18
Province × % Crop	88***	44***	52	38***	85***	27*	77	35	26	31	19
Year	88	45	53	48***	85	45***	77	50***	48***	52***	43***
Year × % Crop	88	45	55	66***	86	57***	77	55*	61***	61***	56***
Year × % Developed	88	49	64**	68	86	58	77	55	61	61	56
Year × % Province	89	49	64	68	86	58	77	64***	63	66**	56
Year × % Crop × Province	89	50	64	69	86	58	77	64	63	66	57
Developed Land 1st											
% Developed Land	11***	15***	29***	10***	4***	18***	15***	<0.1	<0.1	<0.1	<0.1
% Cropland	42***	28***	48***	28***	40***	20	17*	13***	24***	20***	18***
Province	78***	29	50	29	73***	23	75***	35***	25	30***	18
Province × % Crop	88***	44***	52	38***	85***	27*	77	35	26	31	19
Year	88	45	53	48***	85	45***	77	50***	48***	52***	43***
Year × % Developed	88	48	63***	61***	86	52**	77	52	52	54	48*
Year × % Crop	88	49	64	68***	86	58**	77	55	61**	61**	56**
Year × Province	89	49	64	68	86	58	77	64***	63**	66**	56
Year × % Crop × Province	89	50	64	69	86	58	77	64	63	66	57

[a] Omitting high outliers: watershed 240.9 in the wet year and watershed 282 in both years.

least successfully explained by the statistical analysis. Two watersheds showed extremely high concentrations (Fig. 4). One of those was watershed 282 in the Piedmont where the high TNH_4^+ concentrations may come from cattle wastes introduced to the stream near the sampler. Unusually high TNH_4^+ concentrations also occurred at the highly-developed watershed 240.9 for several months during the wet year when the appearance and odor of the water samples suggested possible contamination with sewage. If these anomalous TNH_4^+ concentrations were omitted from the statistical analysis, the main effects of land cover remained significant but the effect of interaction of province with cropland became nonsignificant without the influence of Piedmont watershed 282 (Table 4). Also, when the outliers were dropped, the interaction of year with developed land became significant and the full models explained 64% of the variance (compared to 50% with the outliers included, Table 4).

TABLE 5. Percentages of dissolved ammonium (DNH_4^+), phosphate (DPO_4^{3-}), organic N (DON), organic P (DOP), and organic C (DOC) in TNH_4^+, TPO_4^{3-}, TON, TOP, TOC, respectively. Means (± SE) are for 38 samples in the Coastal Plain and for 49 in the Piedmont. Samples were collected at different stages of flow in the different study watersheds in the Patuxent basin.

	Coastal Plain	Piedmont
DNH_4^+	65 (4.0)	75 (2.4)
DON	63 (4.5)	60 (3.6)
DOC	61 (3.4)	46 (3.2)
DPO_4^{3-}	15 (3.2)	54 (4.1)
DOP	12 (2.0)	24 (3.7)

N, P, and organic C differed in their proportions of dissolved and particulate forms. Comparing grab samples taken from different watersheds at different stages of flow, we found that TNH_4^+ and TON were 60% or more dissolved, while TPO_4^{3-} from the Coastal Plain and TOP from Coastal Plain and Piedmont were generally less than one-fourth dissolved (Table 5). TPO_4^{3-} from the Piedmont was about half dissolved. Organic C averaged 61% dissolved in Coastal Plain discharges and 46% dissolved in Piedmont discharges. The fact that P forms were predominantly particulate means that the P concentrations were correlated with TSS concentrations. The variances of concentrations of TSS and forms of P were statistically related to similar factors (Table 4).

COMPARING INPUTS FROM NPS, PS, AND DIRECT ATMOSPHERIC DEPOSITION

To assess the relative importance of different sources of inputs to the Patuxent estuary, we sep-

TABLE 6. Flow weighted mean concentrations (μg N, P, C, Si, or TSS l^{-1}) in NPS and PS discharges and in atmospheric bulk deposition during the wet and dry years.

	Year	NPS	PS	Atmospheric
TNH_4^+	Wet	82	390	290
	Dry	85	310	580
NO_3^-	Wet	630	4,400	380
	Dry	550	4,900	630
TON	Wet	660	1,100	160
	Dry	520	1,100	420
TN	Wet	1,300	5,900	440
	Dry	1,200	6,400	1,000
TPO_4^{3-}	Wet	220	430	21
	Dry	100	460	65
TOP	Wet	170	81	8.9
	Dry	93	120	25
TP	Wet	400	510	30
	Dry	190	570	89
TOC	Wet	6,800	—	1,500
	Dry	3,700	—	2,900
Si	Wet	5,700	—	—
	Dry	5,000	—	—
TSS	Wet	120,000	2,500	—
	Dry	62,000	2,600	—

TABLE 7. Percentages of the total terrestrial and atmospheric input to the estuary derived from NPS, PS, and direct atmospheric deposition during the wet and dry years.

	Year	NPS	PS	Atmospheric
TNH_4^+	Wet	56	16	28
	Dry	27	20	53
NO_3^-	Wet	66	29	5.8
	Dry	32	58	10
TON	Wet	88	9.3	3.0
	Dry	60	26	14
TN	Wet	75	22	3.7
	Dry	44	46	10
TPO_4^{3-}	Wet	88	11	1.2
	Dry	48	43	8.7
TOP	Wet	96	2.9	0.74
	Dry	75	19	5.8
TP	Wet	92	7.2	0.99
	Dry	58	34	7.7

arately estimated the fluxes from NPS and PS discharges and from direct atmospheric deposition. PS discharges were calculated from reported concentrations and water flows (Papuli and Liang personal communication). Subtracting PS discharges within watershed 251.1 from the measured total discharges yielded estimates of NPS discharges from about 40% of the Patuxent basin. Measured discharges from watershed 235, which included no PS, represent NPS discharges from another 10% of the Patuxent basin. NPS discharges from the remaining half of the Patuxent basin were estimated by using previously described statistical models to predict annual water flow and annual mean material concentrations in discharges from the unmonitored Coastal Plain area. Models to predict concentrations in NPS discharges included only the factors that had $p < 0.1$ in models with either cropland or developed land factors entered first (Table 4). Note that predictions are not affected by the order that factors are entered. The percentage of variance explained by the simplified models was < 4% below the percentage explained by the full models, except for the simplified TNH_4^+ model, which explained 6% less variance than did the full TNH_4^+ model. For predicting TNH_4^+ concentration, we used the model fit to data with the outliers removed. Delivery of materials via atmospheric deposition directly onto the 137-km^2 surface of the estuary was estimated from our measurements of precipitation volume in the Coastal Plain and our measurements of precipitation chemistry at the Rhode River, about 20 km from the head of the Patuxent estuary. To compare concentrations of materials in PS and NPS discharges, we calculated the flow weighted mean concentrations by dividing the total discharge of material by the total discharge of water.

Atmospheric deposition and PS and NPS discharges had strikingly different chemical compositions. Compared to NPS discharges, PS discharges had higher concentrations of N forms and TPO_4^{3-}, but similar concentrations of TOP (Table 6). Atmospheric deposition had TNH_4^+ concentrations similar to or greater than those in PS discharges, and NO_3^- and TN concentrations similar to NPS discharges. Atmospheric deposition had relatively low concentrations of P forms (Table 6). Concentrations of some materials in NPS discharges differed greatly between the wet and dry years. Mean concentrations of P forms, TSS, and TOC were 1.8–2.2 times higher in the wet year than in the dry year. This probably reflects the predominance of particulate forms of P (Table 5) and the tendency of particle concentrations to increase during high flow. Mean concentrations of dissolved Si and forms of N, which are predominately dissolved (Table 5), showed little change between the two years and were no more than 1.3 times higher in the wet year (Table 6).

The importance of PS, NPS, and atmospheric sources differed between the wet and dry years. Although most of the total terrestrial and atmospheric influx came from NPS discharges, these sources did not supply the majority of the total influxes of some N forms during the dry year. In that year, PS were more important than NPS for NO_3^- and TN, while direct atmospheric deposition was most important for TNH_4^+ (Table 7). Direct atmospheric deposition was actually a significant source of TNH_4^+ in both years, supplying 28% of the total annual influx in the wet year and 53% in the dry year. Although TNH_4^+ influx is not a large part of the TN influx, it could have a significant ecological impact on the estuary because of its high biological reactivity. Direct atmospheric deposition was less important for forms of N other than TNH_4^+, supplying no more than 14% of their total annual influxes, and even less important for forms of P, supplying less than 9% of their total annual influxes (Table 7). Differences in the importance of NPS discharges between years were due to changes in water flow (Table 3) as well as changes in concentrations (Table 6).

COMPARING NPS DISCHARGES FROM PIEDMONT AND COASTAL PLAIN

To separate NPS discharges by physiographic province we estimated discharges from the following 5 subwatersheds: Piedmont draining into reservoirs, Piedmont not draining into reservoirs, Coastal Plain within watershed 251.1, Coastal Plain watershed 235, and the unmonitored portion of the Coastal Plain. Watershed 202, because of its small size, was included with the unmonitored portion. Piedmont water flow passing through the reservoirs was calculated from reported flow at the dam on the downstream reservoir (Wright and Wold personal communication). Piedmont water flow not passing through reservoirs was predicted from our statistical model. Concentrations of materials in both components of the Piedmont were predicted from our statistical models. Statistical models were also used to predict discharges from the Coastal Plain portion of watershed 251.1 and from the unmonitored Coastal Plain. Direct measurements of discharge from watershed 235 completed our total of NPS discharges from the Coastal Plain.

In some cases the models predicted unreasonably low concentrations in discharges from the Piedmont subwatersheds. For example, the models predicted negative TPO_4^{3-} concentrations during the wet year and negative Si concentrations during both years in discharges not entering the reservoirs. The predictions of very low or negative concentrations reflect uncertainties in the model and result from extrapolating beyond the land-use compositions of the study watersheds. To eliminate these unreasonable extrapolations we set a lower limit on concentration at the lowest flow-weighted annual mean measured in the study. We substituted this minimum concentration for any predicted concentrations below the minimum. Besides the predictions of negative concentrations mentioned, there were also some predictions of positive concentrations below the lower limit (e.g., for TOC and TON during the dry year). The predicted concentrations for most materials were above the lower limits.

Our data clearly indicate that more of the NPS discharge to the Patuxent estuary came from the Coastal Plain than from the Piedmont. During the study, the Coastal Plain supplied about 80% of the NPS water to the estuary and delivered similar proportions of the NPS TNH_4^+, TN, TOP, and TSS (79%, 80%, 82%, and 83%, respectively). The Coastal Plain delivered greater proportions of the NPS TON, TOC, Si, and total phosphorus (TP; 89%, 90%, 93%, and 95%, respectively) than one would expect based on the proportion of water. The Coastal Plain supplied nearly all of the NPS TPO_4^{3-} (99%). The Coastal Plain supplied only 67% of the NPS NO_3^- because discharges from the Piedmont were richer in NO_3^- than those from the Coastal Plain. The Piedmont delivered 33% of the NPS NO_3^- while delivering only 20% of the NPS water to the estuary. The importance of the Piedmont NPS discharges was reduced due to withdrawal of water from a reservoir. About one-fourth of the total Piedmont NPS water discharge was withdrawn in the wet year and about one-half was withdrawn in the dry year. PS discharges in the Piedmont were negligible, amounting to less than 1% of the PS discharges in the Coastal Plain.

COMPARING NPS DISCHARGES FROM DIFFERENT LAND TYPES

Using our linear statistical models, we estimated the separate contributions of cropland, developed land, and other lands to NPS discharges. The contributions of each land type were estimated separately for each year for each of the following three subwatersheds: the Piedmont draining to reservoirs, the Piedmont not draining to reservoirs, and the Coastal Plain. The contributions were summed across land types, years, and subwatersheds to apportion the total discharges for the entire Patuxent basin.

To estimate the material fluxes from different land types, we first calculated how much each land type contributed to the material concentration in NPS discharge from each subwatershed. The linear model directly estimates the background concentration discharged by all land types and the separate, additive contributions of cropland and developed land to raising concentration above that background concentration. In essence, the model derives a separate regression equation for each province and year. The regression intercept gives the background concentration discharged from all land. The cropland regression coefficient times cropland percentage gives the enhancement above background due to cropland, and the developed land coefficient times developed land percentage gives the additional concentration from developed land.

Sometimes the regression intercept was negative, probably due to uncertainty in predicting low background concentrations. In these cases, we assumed that the minimum background concentration was equal to the lowest annual flow weighted mean concentration measured and that the extra concentration from cropland and developed land was the amount by which the model prediction exceeded the observed minimum. The excess above the assumed minimum was attributed to cropland and developed land in the same proportions as cropland and developed land contribute to elevating the predicted concentration above the regression intercept. For the Coastal Plain we needed to assume a minimum background only for TOP in the wet year and TSS in the dry year. For the Piedmont, we needed to assume a minimum background for all cases except for TNH_4^+ in both years, TOP in the dry year, and TSS in the wet year.

Unlike the other materials, Si concentration decreased with increases in percentage of developed land, so we modeled Si concentration as a function of percentages of cropland and other (not crop or developed) land. Otherwise, the process for apportioning Si concentration among land types was the same as for other materials.

To obtain the flux of material from each land type we multiplied the concentration attributed to the land type times the total NPS water flow from the subwatershed. Total NPS water flow out of the Piedmont draining to the reservoirs is the reported discharge from the lower reservoir. Total water flows from the Coastal Plain and the Piedmont not draining through reservoirs were predicted using the statistical model.

We used a statistical re-sampling approach (the bootstrap, Efron 1982; Crowley 1992) to calculate confidence limits for the estimated proportions of each material originating from the different land types. The data from the 22 studied watersheds were sampled with replacement to construct 10,000 new data sets of 22 watersheds each. For each of the 10,000 data sets, we refit the models for flow and material concentration using the same factors already found to be significant (Tables 2 and 4). We repeated the above calculations of the proportions of material discharge from cropland and developed land.

Some of the 10,000 bootstrap-generated data sets were unsuitable for the calculation. Some generated sets included no study watersheds with significant amounts of developed land, while other sets included none with significant cropland. Such unrepresentative data sets resulted in wildly unrealistic model predictions. We eliminated all generated sets for which the predicted water flow, the predicted background concentration, or the predicted concentrations from developed land or cropland were outside the 95% confidence limits of the same quantities predicted from the actual set of all 22 studied watersheds.

TABLE 8. Percentages of NPS discharges derived from cropland, developed land, and other land during the 2-yr study. Also shown for comparison is the percentage of land cover for the whole watershed. To indicate the uncertainties of the estimates, the 2.5–97.5 percentiles of bootstrap estimates are shown in parentheses. When percentile ranges within a row overlap, they share a common letter in the superscript.

	Cropland	Developed	Other
TNH_4^+	44 (13–61)^{a}	30 (17–40)^{a}	26 (3.6–60)^{a}
NO_3^-	84 (62–90)^{a}	12 (0–19)^{b}	3.7 (0.9–27)^{b}
TON	38 (15–57)^{a}	21 (12–30)^{a}	41 (18–69)^{a}
TN	57 (29–69)^{a}	22 (12–29)^{b}	22 (6.2–49)^{ab}
TPO_4^{3-}	76 (56–90)^{a}	10 (5.8–20)^{b}	14 (1.6–36)^{b}
TOP	73 (43–79)^{a}	21 (14–34)^{b}	5.4 (2.5–37)^{b}
TP	79 (59–86)^{a}	14 (9.2–24)^{b}	7.6 (2.3–28)^{b}
TOC	25 (9.2–51)^{a}	19 (11–29)^{a}	56 (22–79)^{a}
Si	39 (11–52)^{ab}	9.5 (7.2–12)^{a}	52 (41–77)^{b}
TSS	77 (51–82)^{a}	19 (11–34)^{b}	4.2 (2.1–32)^{b}
Cover	10	12	78

Results from the remaining generated data sets define the range of variability in the relative effects of cropland and developed land among samples that are still consistent with the total water discharges and nutrient concentrations predicted by the set of actual study watersheds. Our calculation focuses on the uncertainty in the proportions attributed to cropland and developed land given the total material discharge predicted from the original data set. We used the 2.5th and 97.5th percentiles of results from the remaining generated data sets to define the 95% confidence limits for the percentage of each nutrient attributed to cropland and to developed land (Table 8).

Although cropland covers only 10% of the Patuxent basin, it was the most important source of most materials in NPS discharge. We estimate that cropland supplied about 84% of the of the total NPS discharge of NO_3^-, about three quarters of the TPO_4^{3-}, TOP, TP, and TSS, and about half of the TNH_4^+ and TN (Table 8). Compared to its area, developed land contributed disproportionately large amounts of TNH_4^+, TON, TN, TOP, TOC, and TSS, and a disproportionately small amount of Si in NPS discharges. Other land was the main source of TON, TOC, and Si, but its contribution of these materials was less than its proportion of the total watershed area (Table 8). Bootstrap estimates of 95% confidence limits suggest that, compared to developed land, cropland supplied a significantly higher percentage of the NPS discharges of NO_3^-, TN, TPO_4^{3-}, TOP, TP, and TSS, despite the fact that there was slightly less cropland than developed land in the Patuxent basin (Table 8).

Discussion

TERRESTRIAL AND ATMOSPHERIC SOURCES

The relative importance of PS, NPS, and direct atmospheric inputs to the Patuxent estuary has changed over the past few decades (D'Elia et al. 2003). In the mid-1980s, PS provided the largest inputs of TN and TP to the estuary (Boynton et al. 1995; Sprague et al. 2000), but improvements in sewage treatment have made NPS discharges the dominant nutrient inputs in the late 1990s (Sprague et al. 2000). NPS discharges have also changed as agricultural land area has decreased by 27% while urban land area increased by 21% (Sprague et al. 2000). Our data suggest that conversion of agricultural land to urban land would decrease NPS discharges of most nutrients, but the model used by Sprague et al. (2000) suggests that NPS discharges from watershed 251.1 stayed about the same for TN and decreased slightly for TP from 1985–1998. Direct atmospheric deposition of NO_3^- increased during the 1970s and deposition of TNH_4^+ increased during the 1980s and early 1990s (Correll et al. 1994; Jordan et al. 1995).

Historical trends can be masked by the effects of interannual variations in rainfall, which alter the relative significances of different nutrient sources. PS releases were about the same in both years of our study but NPS releases of TN and TP were respectively 3.7 and 7.2 times higher in the wet year than in the dry year. We also found that direct atmospheric deposition of N becomes more important during periods of low runoff (Table 7), as observed in other estuaries (Correll and Ford 1982; Scudlark and Church 1993).

In the wet and dry years, direct atmospheric deposition accounted for only 3.7% and 10% (respectively) of the total terrestrial and atmospheric influx of TN to the estuary (Table 6), but deposition may still be an important N source to plankton in the estuary. Much of the organic N from the watershed may be refractory, i.e., not readily metabolized by bacteria (Hopkinson et al. 1998). Inorganic N, especially NH_4^+, is most readily available to the phytoplankton. About half of the influx of TNH_4^+ came from direct atmospheric deposition during the dry year (Table 6). Several studies have suggested that direct deposition of inorganic N can be important to estuarine and marine phytoplankton (e.g., Pearl 1985; Owens et al. 1992; Michaels et al. 1993). The importance of atmospheric NH_4^+ to coastal phytoplankton has been demonstrated through isotope analysis (Pearl and Fogel 1994). Even organic N in atmospheric deposition has been shown to stimulate growth of estuarine bacteria and phytoplankton (Seitzinger and Sanders 1999). Indirect inputs of atmospheric deposition are also likely to be important because some deposited N is passed through the watershed. Recent estimates of the percentage of riverine N discharge to Chesapeake Bay derived from atmospheric deposition on land range from 17% (Castro et al. 2001) to 28% (Alexander et al. 2001).

Our study focuses on terrestrial and atmospheric inputs to the Patuxent estuary but nutrients can also enter at the mouth of the estuary from adjacent Chesapeake Bay waters. Budget calculations of Boynton et al. (1995) suggest a net import of 60 Mg P entering the mouth of Patuxent estuary annually. This is equivalent to 12% and 55% of the total inputs of P from terrestrial and atmospheric sources in the wet and dry years of our study respectively. For N, Boynton et al. (1995) calculated an annual net export of 210 Mg N at the mouth, which is equivalent to 10% and 22% of the total inputs of N from terrestrial and atmospheric sources in the wet and dry years of our study respectively. Two other subestuaries of Chesapeake Bay, the Choptank River (Boynton et al. 1995) and Rhode River (Jordan et al. 1991a), import N at their mouths.

NONPOINT SOURCES

Due to unusual rainfall, the annual NPS water discharges we observed differed greatly from long-term averages. Annual water discharges, averaged over 10–47 years, ranged from 36–50 cm yr^{-1} for 5 Coastal Plain watersheds in or near the Patuxent drainage and ranged from 34–43 cm yr^{-1} for 6 Piedmont watersheds in the Patuxent drainage (Carpenter 1983). These long-term averages fall about halfway between the water discharge rates we observed during the wet and dry years of our study (Fig. 3).

Several studies have found that discharges of N and often P increase as the proportion of agricultural land increases (e.g., Neill 1989; Mason et al. 1990; Nearing et al. 1993; Smith et al. 1993; Kronvang et. al. 1995), but some studies have found no apparent effect of agricultural land use on N and P discharges (Owens et al. 1991; Thomas et al. 1992). Since P discharge is related to transport of suspended particles, the influence of agriculture on P discharge may be outweighed by differences in the geochemistry and erodibility of sediments among watersheds (Dillon and Kirchner 1975; Grobler and Silberbauer 1985; Rekolainen 1990; Vighi et al. 1991). Watershed discharges of P are often difficult to quantify because P is strongly associated with suspended particles, which may be discharged primarily during short, unpredictable periods of high flow (Walling and Web 1985; Kronvang 1992). We were able to sample high flow episodes with our automated samplers.

Our previous studies of the Coastal Plain and Piedmont watersheds of Chesapeake Bay found no clear effect of agricultural land on P discharges (Jordan et al. 1997a,b). There were large differences among geographic regions, with the highest P concentrations in discharges from the Rhode River watersheds and the lowest P concentrations in discharges from watersheds in the Piedmont and in the inner and outer Coastal Plain on the Delmarva Peninsula (Jordan et al. 1997a,b). Among the Rhode River watersheds, the watershed with the most cropland discharged the most P (Correll et al. 1992, 1999b; Jordan et al. 1997a), suggesting a possible effect of cropland in that part of the Coastal Plain, as found in the present study for the nearby watersheds of the Patuxent River.

The relationships between TP and TSS concentrations were similar among years and comparable to findings in other years at other watersheds outside of the Patuxent basin. Because most of the P is carried in particulate matter, it is not surprising that the concentration of TP increases with increases in the concentration of TSS. The rate of increase is greater for Coastal Plain watersheds than for Piedmont watersheds (Fig. 6). This implies that the particulate matter discharged from Coastal Plain watersheds is richer in P than is the particulate matter discharged from the Piedmont. This implication is reinforced by the observation that TOP and TPO_4^{3-} are more predominantly in particulate form in Coastal Plain discharges than in the Piedmont discharges (Table 5). A few Piedmont watersheds are exceptional in having TSS and TP concentrations in proportions more typical of the Coastal Plain. One such Piedmont watershed is 282 (Fig. 6), which also showed unusually high concentrations of N forms.

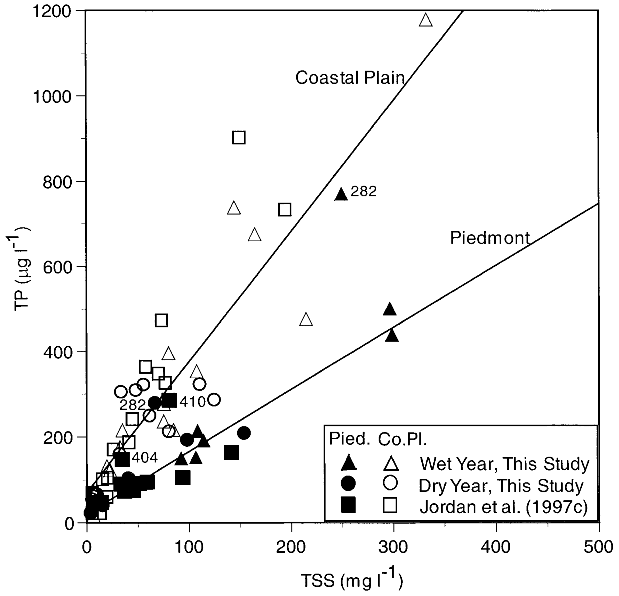

Fig. 6. Annual flow-weighted mean concentration of TP (μg P l^{-1}) versus annual flow-weighted mean concentration of TSS (mg l^{-1}) in discharges from watersheds monitored by Jordan et al. (1997c) and from watersheds monitored in the present study. Triangles represent data from the wet year; circles represent data from the dry year; squares represent data from Jordan et al. (1997c). Filled symbols represent Piedmont watersheds; open symbols represent Coastal Plain watersheds. Lines are fit by linear regression. The upper line is fit to Coastal Plain data. The lower line is fit to the Piedmont data except for data from watersheds 282, 404, and 410 (labeled).

We found that the percentage of cropland was a better predictor of N concentrations in discharge than was the percentage of grassland. Our previous studies found a strong correlation with percentage of cropland but no correlation with the percentage of pastureland (Jordan et al. 1997a,b), and reviews of watershed studies suggest that N discharges from croplands generally exceed those from low-intensity pastures (Beaulac and Reckhow 1982; Frink 1991). Due to livestock waste production, nutrient release from high-intensity pastures can exceed that from croplands (Correll 1996). Livestock waste is a very important source of N in general (Jordan and Weller 1996; Smith et al. 1997) and for the Patuxent watershed in particular (Sprague et al. 2000), but significant proportions of livestock waste N are applied to croplands or escape to the atmosphere as ammonia gas (Jordan and Weller 1996; Jordan et al. 1997a,b). As in the present study, Jordan et al. (1997b) found that Piedmont watersheds release much more N than do Coastal Plain watersheds with similar proportions of cropland. This does not reflect higher loading of N on Piedmont croplands than in Coastal Plain croplands, but instead it may reflect greater retention of nutrients in Coastal Plain riparian buffers or greater leaching of NO_3^- from Piedmont soils (Jordan et al. 1997c).

It is difficult to compare the annual mean concentrations in discharges from watersheds studied in different years because concentrations can change with changes in annual water flow. Concentrations of dissolved Si and forms of N did not differ greatly between the wet and dry years (Table 6) and may be comparable among studies of different watersheds in different years, after accounting for differences in land cover and province. Si and N concentrations measured in the present study were generally similar to those measured in previous studies (Jordan et al. 1997a,b) for watersheds in the same province with similar percentages of cropland.

Watershed 282 in the Piedmont was the only watershed where N concentrations contrasted sharply with those found in our previous studies of Piedmont watersheds (Jordan et al. 1997b). Watershed 282, with about 23% cropland, discharged water with 6.8–7.7 mg l^{-1} NO_3^--N and 8.9–9.3 mg l^{-1} TN concentrations, similar to what our previous findings would suggest for Piedmont watersheds with 60–70% cropland (Jordan et al. 1997b). TNH_4^+ concentrations for watershed 282 were elevated even more, averaging 0.5–0.7 mg l^{-1} TNH_4^+-N while concentrations for other Piedmont watersheds generally averaged less than 0.2 mg l^{-1} TNH_4^+-N (Fig. 4; Jordan et al. 1997b). Concentrations of nutrients (especially TNH_4^+) in the stream draining watershed 282 may have been elevated due to contamination with livestock waste from intensively grazed pastures just upstream of the sampling station where cattle had access to the stream channel. Another possibility is that the EPA-EMAP (1994) estimate of the proportion of cropland in watershed 282 is too low. Unusually elevated N concentrations or inaccurate estimate of cropland percentage at watershed 282 could have a strong influence on the regressions for concentrations of N forms versus cropland in the Piedmont. Because the TNH_4^+ concentrations at watershed 282 were most extreme and most likely to be affected by livestock waste, we omitted those anomalous concentrations from our simplified statistical models used to predict TNH_4^+ concentrations, although we kept other concentration data from watershed 282 in our analyses. Errors in regressions for Piedmont data would not have a large effect on our estimate of total inputs of forms of N to the Patuxent watershed because 67–89% of those inputs come from the Coastal Plain.

Several studies have found that concentrations of nutrients and TSS in watershed discharges increase as the proportion of developed land (or urban land) increases (e.g., Beaulac and Reckhow 1982; Frink 1991). The effects of developed land on NPS discharges are harder to predict than the effects of cropland because the treatment of developed land is usually more varied than the treatment of cropland. There are several possible sources of nutrients in developed land, including septic drainage, sewage system leaks, lawn fertilizers, and industrial activity. The discharges of TSS and associated particulate nutrients may also be increased by enhanced erosion due to accelerated runoff from impervious surfaces in developed lands (e.g., Schueler 1987). Several studies have demonstrated the potential importance of septic drainage as a source of N, especially as leached NO_3^-, in discharge from watersheds (e.g., Valiela et al. 1992; Nizeyimana et al. 1996; Short and Burdick 1996). However, septic systems may not be an important source of P discharge because P becomes bound to the solid substrate (Weiskel and Howes 1992). A comparative study of N leaching suggested that septic systems serving 5 homes per ha would release about as much N per ha as fertilized cornfields but that fertilized lawns were relatively minor sources of leached N (Gold et al. 1990). The relative importance of the different nutrient sources differs among developed watersheds, leading to the potential for idiosyncratic discharge characteristics. The unusually high TNH_4^+ concentrations occurred at the highly developed watershed 240.9 for several months during the wet year suggested sewage contamination. Detailed information about the developed areas, such as density of septic systems and areas of fertilized lawn, would be needed to improve predictions of nutrient discharges. The land cover classification used here (EPA-EMAP 1994) distinguishes between high-density and low-density development, but the proportions of these two land types were highly correlated in our study watersheds. Therefore, we could not differentiate between the effects of different densities of development.

Inaccuracies in land cover data could add uncertainties to our statistical models of NPS discharges. The EPA-EMAP (1994) data we used are the best we have found for the Chesapeake Bay basin, but may include inaccuracies in distinguishing row crops from pasture or other grasslands (Weller et al. 1996, 2003). Improvements in resolving these important land types with remotely sensed data could improve predictions of nutrient discharges. Land cover estimates based on observations in the field are probably more accurate than those based on remotely-sensed data. Field observations of land cover are generally too laborious for large watersheds and were not feasible in the present study.

Changes in land cover may introduce additional uncertainties in modeling nutrient discharges. The EPA-EMAP (1994) land cover estimates are based on data from 1988–1991, but our study measured discharges from 1997–1999. We know that land cover was changing within the Patuxent basin, but we do not know how land cover changed within our study watersheds after the EPA-EMAP (1994) assessment. Also, we do not know how quickly nutrient discharges respond to changes in land cover. A study in the Coastal Plain showed that nutrients carried via groundwater may take several years or decades to emerge in streams (Bohlke and Denver 1995). Discharges of nutrients carried in surface runoff might change more quickly with changes in land cover.

One way to assess the accuracy of our statistical models is to compare measured and model-predicted NPS discharges for a watershed that was not used in constructing the models. Our models did not use data from watershed 251.1 (Fig. 1), which included Piedmont and Coastal Plain lands covering 40% of the Patuxent basin. Model predictions of NPS discharges from watershed 251.1 agreed well with NPS discharges calculated by subtracting reported PS discharges from measured total discharges (Weller et al. 2003).

COMPARING NPS DISCHARGES FROM CROPLANDS AND DEVELOPED LANDS

Our study suggests that greater proportions of the watershed discharges of N and P come from croplands than from developed lands in the Patuxent basin (Table 8). A study of 1998 discharges from watershed 251.1 (Fig. 1) suggested that urban lands accounted for more of the TN and TP discharges than did agricultural lands (Sprague et al. 2000). For comparison we also estimated the percentages of the NPS TN and TP from cropland and developed land in watershed 251.1. Our measurements suggest that croplands release 50% (bootstrap 95% confidence limits: 27–65%) of the NPS TN from watershed 251.1, while developed lands release 34% (19–51%). Sprague et al. (2000) calculate that agricultural lands release only 20% of the NPS TN while urban lands release 73%. Note that they report release from agricultural lands, which would include pasture and hayfields as well as croplands. Despite including those extra land types, their estimated release from agricultural lands falls below the confidence limits of our estimated release from croplands. Their estimated release from urban lands, including urban runoff plus septic releases, is above the confidence limit of our estimate for developed lands. Our attribution of NPS TP sources agrees more closely with Sprague et al. (2000). We estimate that croplands release 46% (31–56%) of the TP while developed lands release 44% (32–60%). Sprague et al. (2000) estimate that agricultural land releases 43% of the TP while urban land releases 56%.

To prioritize efforts to reduce NPS pollution, it is obviously important to determine which land types contribute the most. Sprague et al. (2000) estimate the contributions of different NPS sources based on the Hydrologic Simulation Program-FORTRAN (HSPF) model of Bicknell et al. (1997). This model is widely used and supported by the U.S. Environmental Protection Agency, U.S. Geological Survey, and U.S. Army Corps of Engineers (Sprague et al. 2000). The model is calibrated by adjusting a large number of physical parameters to provide the best agreement between observed and predicted discharges from several watersheds of Chesapeake Bay. The adjusted parameters from the calibrated model are used in making inferences about the sources of NPS discharges (Sprague et al. 2000). Our approach is more empirical, using simple regressions of land cover percentages versus concentrations of materials discharged from watersheds that represent a range of land cover composition. The contradictory conclusions of our approach and the HSPF model concerning the NPS TN release from agricultural and urban lands suggests that the inferences based on the HSPF parameters should be re-examined.

Conclusions

In addition to providing current measurements of inputs of nutrients and sediments into the Patuxent River estuary, our study provides a basis for several inferences about the factors that control these inputs. The effects of interannual variation in precipitation are illustrated by comparing wet and dry years. Annual flow-weighted mean concentrations of TSS, organic C, and forms of P were higher in the wet year by about a factor of 2 (Table 5), while mean concentrations of Si, NO_3^-, TNH_4^+, and TN did not differ significantly between years (Table 4). Differences in annual precipitation also altered the relative importance of NPS, PS, and atmospheric sources of nutrients, with NPS becoming more important in wetter years, and atmospheric sources of N becoming more important in drier years. Our study has also provided more data indicating important differences in discharges from Piedmont and Coastal Plain watersheds. Piedmont watersheds tend to discharge more N than do Coastal Plain watersheds, and Piedmont discharges tend to have a lower ratio of TP to TSS than do Coastal Plain discharges. Our data also suggest that croplands release more NPS N and P per area than do developed lands.

ACKNOWLEDGMENTS

This study was funded by grants from the National Oceanic and Atmospheric Administration (NA66RG0129), the National Science Foundation (DEB-93-17968), and the Smithsonian Institution Environmental Sciences Program. Laboratory and field work was carried out by several technicians including: Keith Bayha, Mark Carroll, James Duls, Sarah Eppley, Helen Hall, Liza Hamill, Brian Kulak, Joseph Miklas, and Leonard Tabor. Nancy Goff supervised the technicians and assisted with data management.

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Received for consideration, July 31, 2001
Revised, May 29, 2002
Accepted for publication, June 14, 2002