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Base Flow Nutrient Discharges from Lower Delmarva Peninsula Watersheds of Virginia, USA

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Proper management of shallow coastal systems, which are vulnerable to nutrient enrichment, requires knowledge of land use impacts on nutrient discharges. This study quantified base flow nutrient concentrations and yields for 1 yr (May 2001–April 2002) from 14 first-order streams on the Virginia Eastern Shore (VaES) on the Delmarva Peninsula and assessed their relationships with land cover and soil drainage class in their watersheds. Base flow water discharge rates (1.4–31.5 cm yr^{-1}) were likely lower than the long-term average due to a severe drought. Seasonal mean nitrate concentrations were higher in winter, while mean dissolved organic carbon and ammonium concentrations were higher in summer. Annual base flow-weighted mean total dissolved nitrogen (TDN) concentrations were positively related to percent (%) agricultural land cover ($r^2 = 0.43$; $p = 0.02$) and % very poorly drained soils ($r^2 = 0.51$; $p = 0.009$) and negatively related to % forested land cover ($r^2 = 0.54$; $p = 0.005$). Patterns of base flow TDN yields were similar to those of concentrations but were also positively related to % developed land cover ($r^2 = 0.40$; $p = 0.03$). Agricultural and developed land covers, together with very poorly drained soil, accounted for 91% of the variability of TDN yields ($p = 0.0001$). Using a multiple regression model, the base flow TDN loading rate to a coastal lagoon on the VaES, a system vulnerable to nutrient enrichment, was estimated to be 28,170 kg N yr^{-1}.

Eutrophication of coastal ecosystems is a growing problem worldwide due to increased population pressure and associated disturbances to air, land, and water. Land use changes in watersheds and nutrification of the shallow aquifer can promote increased release of nutrients to coastal waters that support excess primary production, including blooms of phytoplankton, ephemeral macroalgae, and harmful algae (Howarth et al., 2002). Respiration of the excess organic matter (OM) produced can result in oxygen depletion (hypoxia and anoxia) and subsequent fish and shellfish mortalities (Valiela et al., 1997). With respect to coastal lagoons or bays located on the seaside of Virginia's Eastern Shore (VaES), comprising the southern portion of the Delmarva Peninsula, sporadic blooms of opportunistic macroalgae have been documented (McGlathery et al., 2001). In Hog Island Bay (HIB), diebacks and decomposition of macroalgae have led to localized areas of anoxia/hypoxia during the summer. Nitrate-enriched ground water is suspected of contributing to these blooms in Virginia's coastal lagoons. Experimental evidence indicates that nitrogen (N) is the key limiting nutrient for macroalgal and phytoplankton growth in most shallow coastal water systems (Pedersen and Borum, 1996).

Ground water contributions to coastal water bodies can occur as base flow, defined as ground water discharge to non-tidal portions of streams, or as direct discharge into tidal coastal waters. In studies conducted in the mid-Atlantic Coastal Plain (Bachman et al., 1998) and specifically in the upper Delmarva Peninsula of Maryland (MD) and Delaware (DE) (Jordan et al., 1997a; Phillips and Bachman, 1996; Bohlke and Denver, 1995), base flow contributed on average between 60 and 80% of total stream flow and represented a significant source of N to low-order streams. Although studies conducted in the VaES have examined relationships between watershed characteristics and nutrient concentrations in ground water and in direct ground water discharge to coastal waters (Speiran, 1996; Reay et al., 1992; Reay, 2004), little information is available on the importance of base flow contributions of water and nutrients to coastal waters, in particular to seaside coastal lagoons.

Land use in watersheds has been shown to affect nutrient concentrations in surface and ground water. Within the mid-Atlantic Coastal Plain, annual N inputs to shallow ground water from row-crop land use are on the order of 20 to 30 kg ha^{-1}, and subsurface losses of N can represent 75 to 90% of the total N runoff from agricultural fields (Peterjohn and Correll, 1984; Lowrance, 1992).

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Abbreviations: DIN, dissolved inorganic nitrogen; DOC, dissolved organic carbon; DON, dissolved organic nitrogen; FW, flow-weighted; HIB, Hog Island Bay; OM, organic matter; TDN, total dissolved nitrogen; VaES, Virginia Eastern Shore; VCR-LTER, Virginia Coast Reserve- Long Term Ecological Research.

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In contrast, annual N inputs from forested lands are generally less than 5 kg ha^{-1} (Gold et al., 1990; Valiela et al., 1997). Ground water N yields from septic systems vary from 4.2 to 10.7 kg $household^{-1}$ yr^{-1}, which equates to 10.5 to 26.8 kg ha^{-1}, assuming 1-acre zoning (Gold et al., 1990; Valiela et al., 1997; Reay, 2004). Ground water studies conducted on the Delmarva Peninsula have documented elevated concentrations of nitrate (NO_3^-) or ammonium (NH_4^+) underlying agricultural and residential areas utilizing septic systems, with dissolved inorganic N (DIN) concentrations varying from 385 to 710 μmol L^{-1} (Reay et al., 1991; Denver et al., 2004) and 4494 μmol L^{-1}, respectively (Reay, 2004). In comparison, reported ground water DIN concentrations underlying forested lands vary from 28 to 89 μmol L^{-1} (Jordan et al., 1993; Reay et al., 1991). Forested lands down-gradient of land uses with high N yields often exhibit elevated ground water N levels immediately adjacent to that land use or deeper within the water table aquifer as a result of ground water bypassing the biologically active zone (Hamilton et al., 1993).

Soil characteristics in watersheds can also affect ground water N concentrations and speciation. In the Coastal Plain, riparian forests typically have poorly drained soils, which can potentially facilitate removal of N from ground water via plant uptake and denitrification, with estimated forest N removal/retention rates of 70 to 90% (Peterjohn and Correll, 1984; Jordan et al., 1993; Lowrance et al., 1997). In contrast, in well drained soils of the Delmarva Peninsula, NO_3^- has been shown to persist due to relatively high dissolved oxygen levels, the lack of carbon substrate, and limited microbial denitrifier populations (Parkin and Meisinger, 1989). This is of particular concern in agriculturally dominated watersheds.

Shallow coastal systems, such as those on the VaES, are vulnerable to anthropogenic disturbances resulting in nutrient enrichment. Proper management of such systems requires knowledge of watershed characteristics and their relationships to N yields. Relationships between land cover in watersheds and base flow nutrient concentrations, information important for prediction of nutrient yields, have not been determined for the VaES. With those needs in mind, the objectives of this study were (i) to characterize and quantify base flow nutrient concentrations and discharges in 14 streams distributed along a north-south transect, (ii) to determine relationships between watershed characteristics and base flow nutrient concentrations and yields, and (iii) to provide a first-order estimate of annual base flow total N loading to HIB, a coastal bay on the VaES.

Materials and Methods

Virginia Eastern Shore Study Area Description

The VaES on the lower Delmarva Peninsula forms the eastern shore of the Chesapeake Bay (Fig. 1) and is located in the outer Coastal Plain physiographic region. It generally has flatter topography, a deeper unconfined aquifer, and less stream incision than inner Coastal Plain regions (Correll et al., 1992). The VaES is approximately 100 km long and 5 to 20 km wide. As a result of the relatively narrow width of the VaES, watershed catchments and stream inputs to coastal waters are generally smaller than in northern areas of the Delmarva Peninsula and the western shore of Chesapeake Bay. The eastern half of the VaES has an area of 1540 km^2 and is part of the Virginia Coast Reserve–Long Term Ecological Research site (VCR-LTER). Approximately 56 major streams drain the seaside of the VaES into the shallow lagoons that separate the mainland from 14 barrier islands (Hayden and Porter, 2001). Land cover on the VaES is approximately 38% agriculture, 32% forest, 27% wetlands, and 2% developed. Poultry farming is an especially important activity in Accomack County, the northern half of the VaES, which had 77 farms and more than 31.7 million broiler chickens raised in 2002, whereas the southern county (Northampton) had reported none (USDA, 2002). Wheat, soybean, corn, tomato, and other vegetables are prevalent crops grown on the VaES.

The fresh ground water system of VaES consists of the unconfined, water table Columbia aquifer and the underlying confined Yorktown-Eastover aquifers (upper, middle, and lower), which are separated by intervening confining units (Richardson, 1994). The water table aquifer is recharged locally by rainfall and flows laterally from the center divide on the peninsula east toward the coastal lagoons and west toward the Chesapeake Bay. The confining unit of the upper Yorktown-Eastover limits vertical ground water movement between aquifers, resulting in 86 to 92% of the water moving laterally through the unconfined aquifer. Ground water is discharged into springs, streams, marshes, and lagoons and directly into the Chesapeake Bay and Atlantic Ocean.

Stream Selection and Watershed Data Analysis

Fourteen first-order streams on VaES were selected for base flow measurements based on the following criteria: year-round measurable flow, relative percentage of forest and agricultural land cover in the watershed, no known point source discharges, and site accessibility (Fig. 1). Sampling sites were located upstream of the stream's mouth and therefore did not include all contributing base flow from the entire creek. Selected streams were distributed latitudinally along the eastern half of the VaES over a distance of 70 km. We used Geographic Information Systems (ArcView and ArcInfo, ESRI, Redlands, CA) to delineate watersheds at the sampling points and to determine watershed percentages of land cover and soil drainage class. Watershed boundaries were digitized by examining elevation data on USGS 7.5-min mylar topographic quadrangle maps (1:24,000). Stream (watercourse channel) length was determined by summing the lengths of natural or artificial channels, which periodically or continuously contain moving water, above the stream sampling points identified on USGS 7.5-min maps. Land cover percentages were based on 1988–89 National Oceanic and Atmospheric Administration Coastal Change Analysis Program (NOAA CCAP) land cover data (1:24,000 scale). To simplify statistical analyses, nine land cover classes found in the watersheds were grouped into three major land cover categories: agriculture (i.e., cropland, grassland), forest (i.e., forests, scrub/shrub), and developed land (i.e., low- and high-intensity developed land). Cropland, specifically winter wheat, is frequently mistaken for grassland; selected ground-truthing found that areas

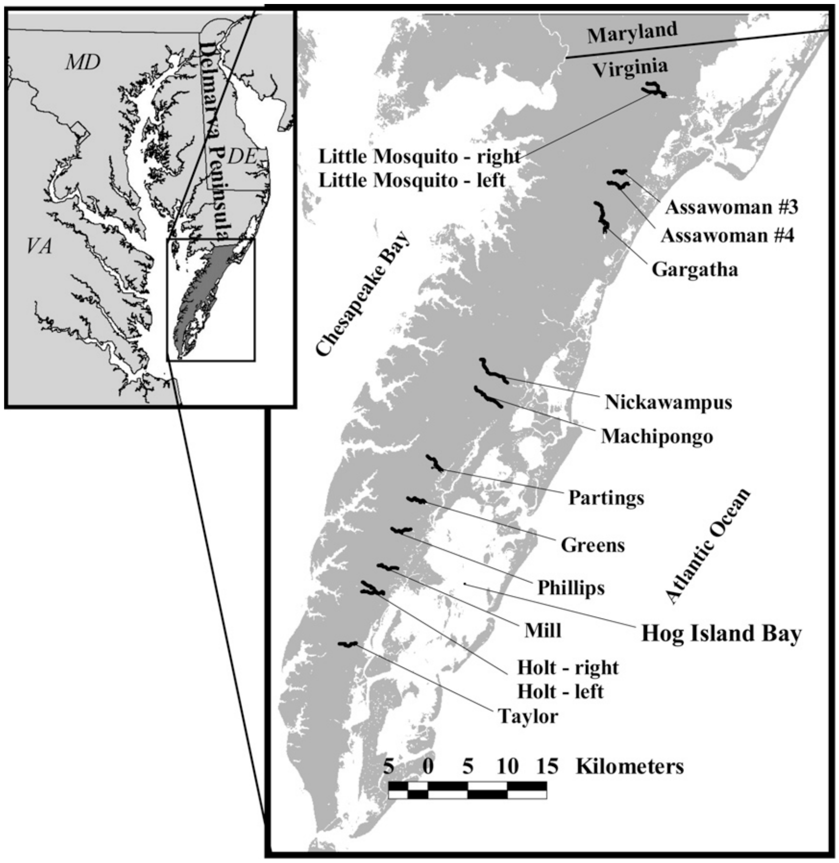

Fig. 1. Map of the 14 sampled streams and Hog Island Bay on the Virginia Eastern Shore, which is located on the lower Delmarva Peninsula.

classified as grassland were most likely cropland. Soil type was determined using the USDA Soil Survey Geographic (SSURGO) database (1:15,840 scale) and soil drainage class for each soil type from USDA Soil Surveys for Northampton and Accomack counties (Cobb and Smith, 1989; Peacock and Edmonds, 1994). Soil drainage classes were grouped into three major categories: well drained (i.e., well drained, moderately well drained, somewhat excessively drained), poorly drained (i.e., poorly drained, somewhat poorly drained), and very poorly drained. Watershed area, % land cover, and % soil drainage classes in the study watersheds are presented in Table 1.

Sampling and Analytical Methods

Streams were sampled monthly from May 2001 through April 2002. To focus on base flow conditions and to exclude interference from surface water runoff, samples were collected only when there was at least a 48-h antecedent period of no precipitation. Water samples in triplicate were collected above the zone of tidal influence and upstream of the nearest road, filtered (Pall 0.45-μm Acrodisc Supor; Pall Corporation, Ann Arbor, MI), and frozen until analyzed for NO_3^-, nitrite (NO_2^-), NH_4^+, total dissolved N (TDN), orthophosphate (PO_4^{3-}), and dissolved organic carbon (DOC). Ancillary field data collected (YSI 30M; YSI Inc, Yellow Springs, OH) included temperature and specific conductivity. Daily regional rainfall data were obtained from local NOAA weather stations in Eastville, Painter, and Wallops Island, VA (NOAA, 2005) and the VCR-LTER station in Phillips Creek, VA (Krovetz et al., 2002). Additional rain gauges (Davis Instruments rain collector [Davis Instruments, Hayward, CA] with a HOBO Event Recorder [Onset Computer Corporation, Bourne, MA]) were installed at four study sites for specific portions of the study period to measure instantaneous rainfall and to verify that local precipitation events did not occur before sampling.

Nitrate and NO_2^- were analyzed using an Alpkem "Flow Solution" autoanalyzer (Perstorp, 1992), NH_4^+ was analyzed by the phenol hypochlorite method (Solorzano, 1969), and TDN was analyzed by analysis of DIN after digestion by alkaline persulfate in sealed ampules (Grasshoff et al., 1983). Dissolved organic N (DON) was derived by subtracting DIN (NH_4^+ + NO_3^- + NO_2^-) from TDN. Ortho-phosphate was analyzed by the molybdate method (Parsons, 1984). Dissolved organic C was analyzed using a Shimadzu TOC-5000A analyzer (Shimadzu Scientific Instruments, Columbia, MD).

Base Flow Discharge Rate, Flow-Weighted Mean Nutrient Concentration, and Nutrient Yields

Instantaneous discharge rates ($m^3\ s^{-1}$) under base flow conditions were measured monthly using the mid-section method (Rantz et al., 1982). Given the shallow stream depths (range of maximum depths: 5.6–35.1 cm), surface flow velocity was measured with a surface float and adjusted (multiplied by 0.85) to estimate mean vertical velocity as described by Rantz et al. (1982). Instantaneous discharge rates ($m^3\ s^{-1}$) were assumed to

Table 1. Watershed area, stream length, land cover, soil drainage class, mean daily base flow discharge rate ($m^3\ d^{-1}$), and annual base flow water discharge rate normalized by watershed area for the 14 study watersheds.

Watershed ID	Area	Stream length	Land cover			Drainage class			Base flow discharge	
			DEV†	FOR	AGR	VPD	PD	WD	Daily	Annual
	ha	m	%			%			$m^3\ d^{-1}$	$cm\ yr^{-1}$‡
Little Mosquito-R	206.5	2351	<0.1	58.6	41.4	5.4	43.0	51.6	1589.0	28.1 ± 1.7
Little Mosquito-L	185.9	2174	0.0	57.5	42.4	2.9	54.1	42.8	73.3	1.4 ± 0.2
Assawoman #3	111.7	1680	1.3	29.3	69.2	12.4	2.7	84.9	559.2	18.2 ± 0.6
Assawoman #4	155.5	1939	1.3	51.3	47.3	11.2	30.8	58.0	225.9	5.3 ± 0.4
Gargatha	393.6	2745	4.1	37.2	58.7	5.9	24.3	31.6	2004.5	18.7 ± 1.4
Nickawampus	180.5	2879	13.5	24.6	61.9	15.0	25.7	59.4	1554.7	31.5 ± 1.3
Machipongo	186.8	1385	0.4	46.3	53.3	<0.1	48.8	51.2	231.9	4.5 ± 0.5
Partings	190.7	1711	9.8	44.6	45.4	1.7	49.6	48.2	875.9	16.7 ± 1.3
Greens	238.0	1671	4.0	67.5	28.5	4.7	42.4	52.7	870.0	13.3 ± 0.5
Phillips	116.3	1439	0.5	34.4	65.1	1.9	37.0	60.5	339.7	10.6 ± 1.7
Mill	171.1	1097	1.9	66.6	31.5	2.1	27.8	68.7	189.0	4.0 ± 0.6
Holt-R	171.6	2224	0.6	24.3	75.1	3.8	35.2	61.0	682.3	14.5 ± 1.8
Holt-L	100.1	1847	0.7	37.1	62.1	2.9	29.8	67.3	396.5	14.4 ± 1.8
Taylor	209.9	1900	0.3	42.2	57.4	<0.1	8.6	91.4	1278.0	22.2 ± 1.2

† AGR, agriculture; DEV, developed; FOR, forest; L, left branch; PD, poorly drained; R, right branch; VPD, very poorly drained; WD, well drained.

‡ 1 cm = 100 $m^3\ ha^{-1}$; ±SE.

represent the average base flow discharge rate throughout the month, and monthly rates were summed to estimate annual base flow discharge rates ($m^3\ yr^{-1}$). Annual base flow nutrient yields, expressed as $kg\ ha^{-1}\ yr^{-1}$, for each stream were calculated by multiplying monthly nutrient concentrations by monthly discharge rates, summing monthly nutrient loads (kg) over 1 yr, and dividing by watershed area (ha). Annual base flow-weighted (FW) mean nutrient concentrations ($\mu mol\ L^{-1}$), calculated by dividing the total annual base flow nutrient loads by the total annual base flow discharge rates, were determined to examine water quality patterns independent of water discharge.

Statistical Analyses

StatView 5.0 for Windows (SAS Institute Inc., Cary, NC) was used to perform all statistical analyses. Repeated-measures ANOVA was conducted on seasonal mean nutrient concentrations to determine differences by season. The following months of data were averaged to represent seasonal means: spring, March through May; summer, June through August; fall, September through November; and winter, December through February. Seasonal means were found to have similar variances by Levene's test of homogeneity of variance ($p > 0.05$). Tukey's test was used to evaluate pairwise comparisons. Relationships between annual FW nutrient concentrations and yields and percentages of land cover and soil drainage type in watersheds were analyzed by simple linear and stepwise multiple regression analyses. Factors with significant correlations were not included together in multiple regressions due to concerns about multi-collinearity.

Because water quality and discharge were measured only once per month, standard error estimates for normalized annual base flow discharge rates, FW mean nutrient concentrations, and yields were calculated using the method of collapsed strata with one unit per stratum (Sukhatme et al., 1984). This technique, which makes it possible to obtain an approximate and likely overestimate of the variance, determines the variance by grouping together pairs of strata (measurements made in two successive months), calculating the variance of each pair, and summing them together. A stratum was defined as 1 mo.

Results

Watershed Characteristics and Base Flow Discharges

Upper first-order stream watersheds varied in area from 100.1 to 394.6 ha, with associated stream lengths varying from 1097 to 2879 m. Drainage density, defined as stream length per watershed area, was low for all watersheds (range, 0.6–1.9 $km\ km^{-2}$). Areal percentages of forested and agricultural land covers varied from 24.3 to 67.5% and 28.5 to 75.1%, respectively, between watersheds (Table 1). Only two watersheds (Nickawampus and Partings Creek) exhibited greater than 5% developed lands. In all but two watersheds (Nickawampus and Machipongo), forests were the dominant land cover immediately adjacent (<6 m) to the streams. As with land cover, soil drainage characteristics varied between watersheds, with well drained and poorly drained soils ranging from 31.6 to 91.4% and 2.7 to 54.1%, respectively (Table 1). Very poorly drained soils, which were commonly present in depressions and/or along streams, accounted for <0.1 to 15.0% of area. As expected, watersheds dominated by agricultural lands typically exhibited elevated areal percentages of well drained soils.

This study occurred during a drought that directly affected base flow discharge rates and patterns. For the study period, the average total precipitation for all sites (84.5 cm) was approximately 77% of the 50-yr long-term average at the Painter station (110.2 cm) (NOAA, 2005). Although local precipitation patterns were somewhat variable, particularly during the initial part of the study (May–July 2001), below-average rates generally occurred between August 2001 and March 2002. The Palmer-Drought Severity Index for the Tidewater region of Virginia decreased from 0 to −2 from April to September 2001, indicating a change from normal to moderate drought conditions (NOAA, 2003). From October 2001 to April 2002,

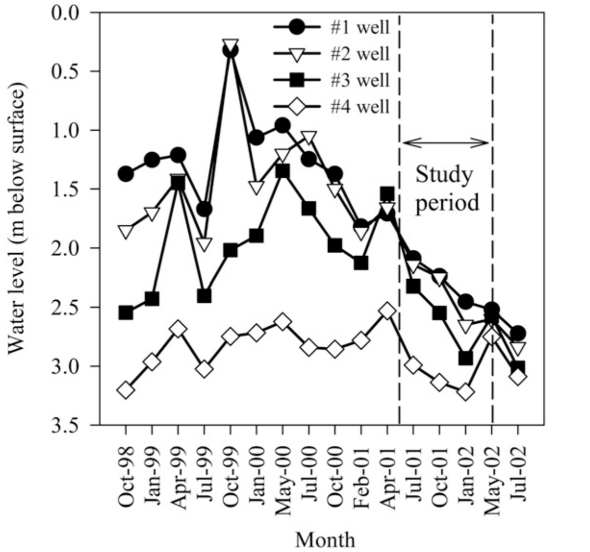

Fig. 2. Ground water levels below surface (m) for wells in Northampton (#1, #2) and Accomack (#3, #4) counties (Virginia Department of Environmental Quality, 2002). Wells were installed within the water table aquifer to depths below the land surface of 3.9 m for well #1, 21.3 m for #2, 11.3 m for #3, and 15.2 m for #4.

the index ranged from −2 to almost −4; −3 is indicative of severe drought and −4 of extreme drought. A consequence of drought was an overall low recharge of the water table aquifer, as supported by water level data of monitoring wells measured within the water table aquifer on VaES (Fig. 2). Water table elevations continued to decline from October 2001 through January 2002, failing to exhibit a more typical recharge period associated with this time period of the water year.

Volumes and patterns of base flow varied among watersheds (Table 1 and Fig. 3a). Mean daily base flow discharge ranged from 73.3 $m^3 d^{-1}$ (Little Mosquito-L) to 2004.5 $m^3 d^{-1}$ (Gargatha Creek). Annual base flow discharge ($m^3 yr^{-1}$) was not strongly correlated with drainage density, % land cover, or % soil drainage class; however, it was significantly related to watershed area and stream length (Fig. 4). Watershed area and stream length accounted for 68% of the variability of annual base flow discharge (p = 0.002; Eq. [1]).

Annual base flow discharge ($m^3 yr^{-1}$) = 227.0 × stream length (m) + 1401.1 × watershed area (ha) − 416,996 [1]

To remove the effect of watershed area, base flow discharge rate was divided by watershed area (1 cm = 100 $m^3 ha^{-1}$). No significant correlations were found between annual normalized discharge rates and drainage density, % land cover, or % soil drainage class. Annual normalized base flow discharge varied from 1.4 to 31.5 cm yr^{-1}, representing approximately 2 to 37% of the rainfall that occurred during that period. Seasonal patterns of normalized daily base flow discharge observed between watersheds were highly variable and in many cases did not demonstrate the typical hydrograph pattern of low summer/early fall base flow followed by increasing flow from late winter to early spring as a result of reduced evapotranspiration demands and elevated water table aquifer recharge (Fig. 3b). The higher-than-expected flow in summer/early fall compared with the winter recharge period in many of the streams is likely due to the above average rainfall in July followed by drought in the fall.

Base Flow Nutrient Concentrations and Yields

Summary data of monthly base flow NO_3^-, NO_2^-, NH_4^+, DON, PO_4^{3-}, and DOC concentrations for the 14 creeks assessed in this study are presented in Fig. 5. Nitrate concentrations averaged over the study period ranged from 3.4 to 313.3 µmol L^{-1}, with the exception of Assawoman #4, which had a mean concentration of 528.8 (±94.1) µmol L^{-1} and individual high values of 1040.8 and 1197.3 µmol L^{-1} observed, respectively, in December and August 2001. For all streams,

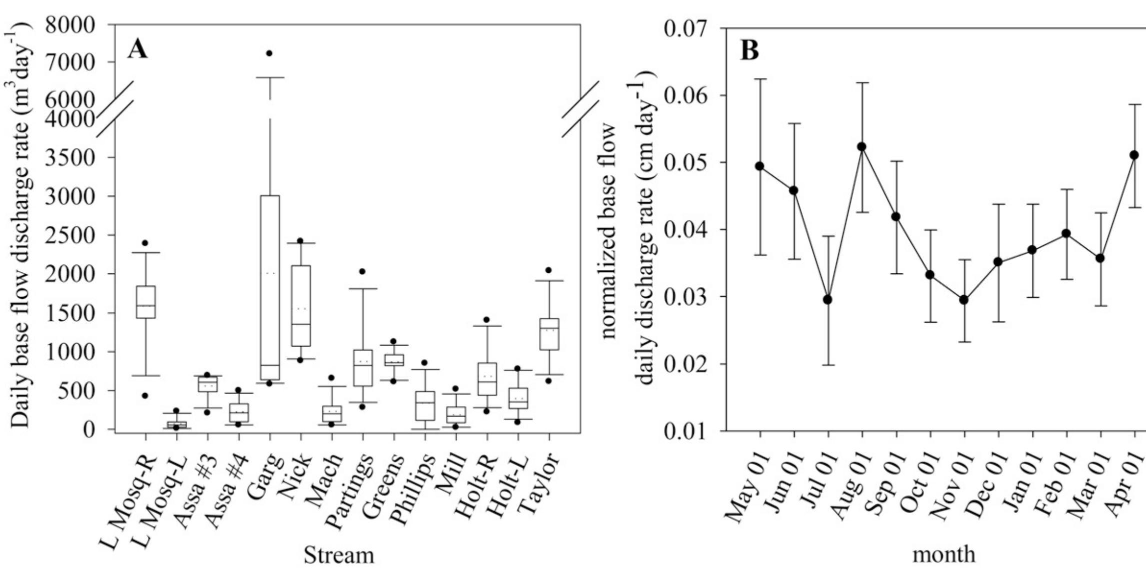

Fig. 3. (A) Box plot of daily base flow discharge rates ($m^3 d^{-1}$) measured monthly. The boxes represent 25th and 75th percentiles, and whiskers correspond to 10th and 90th percentiles. Dotted line is mean, solid line is median, and circles are minimum and maximum. (B) Mean daily base flow discharge rates, normalized by watershed area (cm d^{-1}; ±SE), for all streams each month (n = 14).

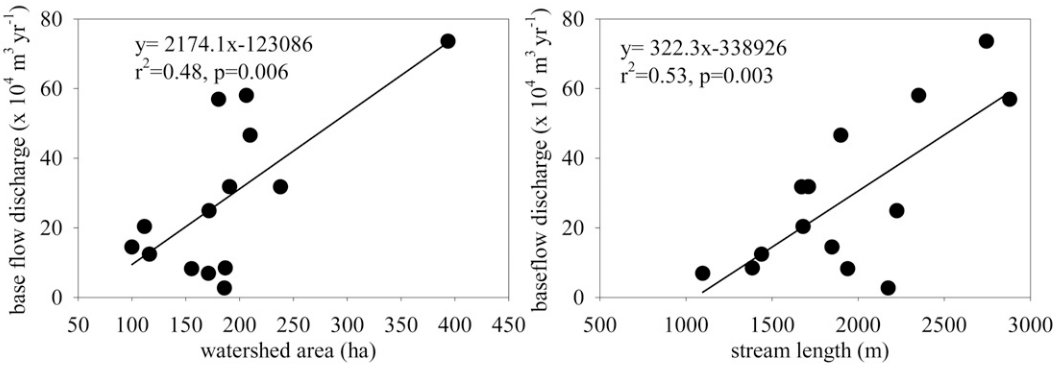

Fig. 4. Annual base flow discharge rate ($m^3\ yr^{-1}$) versus watershed area (ha) and stream length (m) (n = 14).

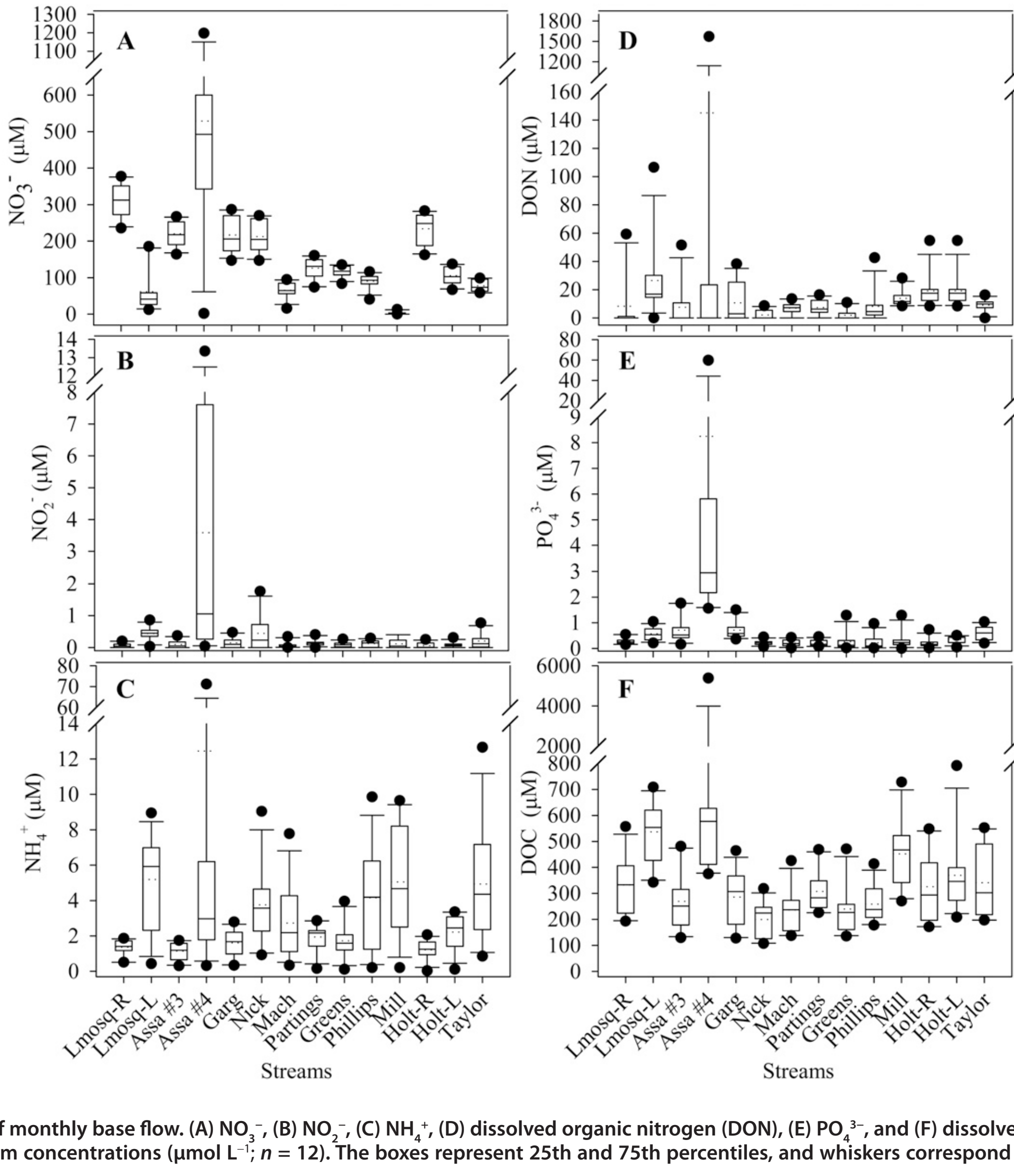

Fig. 5. Box plot of monthly base flow. (A) NO_3^-, (B) NO_2^-, (C) NH_4^+, (D) dissolved organic nitrogen (DON), (E) PO_4^{3-}, and (F) dissolved organic carbon (DOC) stream concentrations ($\mu mol\ L^{-1}$; n = 12). The boxes represent 25th and 75th percentiles, and whiskers correspond to 10th and 90th percentiles. Dotted line is mean, solid line is median, and circles are minimum and maximum.

except Mills Creek (15%), NO_3^- was the dominant N species, comprising 66 to 98% of the TDN pool. In contrast, mean NO_2^- and NH_4^+ concentrations were low (range, 0.1–0.4 $\mu mol\ L^{-1}$ and 1.2–5.1 $\mu mol\ L^{-1}$, respectively), with the exception of Assawoman #4, which had mean concentrations of 3.6 (±1.4) $\mu mol\ L^{-1}$ for NO_2^- and 12.5 (±6.6) $\mu mol\ L^{-1}$ for NH_4^+ and an individual high NH_4^+ value of 71.2 $\mu mol\ L^{-1}$ in May 2001. The contribution of NH_4^+ to the TDN pool was 6% or less for all streams except Mill Creek (22%). Mean DON levels within the study streams ranged from 2.0 to 26.5 μmol L^{-1}. As with NO_3^-, NH_4^+, and PO_4^{3-}, Assawoman #4 Creek exhibited the highest mean DON concentration (145.1 ± 130.1 μmol L^{-1}), with a single value exceeding 1500 μmol L^{-1} (July 2001). Mean PO_4^{3-} concentrations were relatively low (≤0.7 μmol L^{-1}) for all streams except for Assawoman #4, which exhibited a mean concentration of 8.3 ± 4.7 μmol L^{-1} and single peak value of 59.7 μmol L^{-1} (July 2001). Mean stream DOC concentrations varied from 199.6 ± 20.0 for Nickawampus Creek to 536.2 ± 33.2 μmol L^{-1} for Little Mosquito-L Creek, except for Assawoman #4 Creek, which had a mean DOC concentration of 934.5 ± 405.6 μmol L^{-1} and a peak concentration of 5381 μmol L^{-1} in July 2001.

Annual FW mean nutrient concentrations and yields for the 14 streams in this study are presented in Tables 2 and 3. Flow-weighted concentration ranges were 2.6 to 566.2 μmol L^{-1} for NO_3^-, 1.1 to 16.8 μmol L^{-1} for NH_4^+, 2.0 to 52.9 μmol L^{-1} for DON, 22.8 to 641.0 μmol L^{-1} for TDN, 0.2 to 5.3 μmol L^{-1} for PO_4^{3-}, and 220.7 to 657.2 μmol L^{-1} for DOC. Annual yield ranges were 0.01 to 12.63 kg N ha^{-1} for NO_3^-, 0.01 to 0.18 kg N ha^{-1} for NH_4^+, 0.05 to 0.56 kg N ha^{-1} for DON, 0.13 to 12.87 kg N ha^{-1} for TDN, 0.002 to 0.084 kg P ha^{-1} for PO_4^{3-}, and 0.91 to 10.36 kg C ha^{-1} for DOC. Compared with the other creeks in this study, Assawoman #4 was distinguished by its high and variable nutrient and DOC concentrations (Table 2) and by its high mean specific conductivity (731 ± 40 μS) compared with the other creeks (range of means, 172–297 μS). This creek was also listed as impaired waters on the Virginia 2006 305(b)/303(d) Integrated Report due to *Escherichia coli* and fecal coliform contamination (VADEQ, 2006). Because these results suggested a possible local source of wastewater discharge to Assawoman #4, we excluded this creek from further nutrient analysis.

When examining relationships between various base flow nutrient species, we found that annual FW NO_3^- concentrations were negatively correlated with NH_4^+ ($r^2 = 0.44$; $p = 0.01$); FW DOC and DON concentrations were positively correlated with each other ($r^2 = 0.62$; $p = 0.002$). When analyzing seasonal differences, we observed that mean NO_3^- concentrations for the 13 streams were significantly higher in winter compared with other seasons ($F = 10.50$; df = 3, 36; $p < 0.0001$) (Fig. 6A); conversely, mean DOC ($F = 27.19$; df = 3, 36; $p < 0.0001$) and NH_4^+ ($F = 5.22$; df = 3, 36; $p = 0.004$) concentrations were significantly higher in summer (Fig. 6B and 6E). Mean PO_4^{3-} concentrations demonstrated a similar seasonal pattern as NH_4^+, although means were not significantly different among seasons ($F = 2.85$; df = 3, 36; $p = 0.051$) (Fig. 6D). Higher mean DON concentrations were found in the spring ($F = 4.32$; df = 3, 36; $p = 0.01$) (Fig. 6C).

Relationships between annual base flow FW NO_3^- and TDN concentrations, yields, land cover, soil type, and drainage class were determined by single and multiple regression analyses (Tables 4 and 5). Through studentized deleted residual analysis of NO_3^- and TDN regressions, Little Mosquito-R Creek was identified as an outlier (studentized residuals greater than ±4) and was excluded from further NO_3^- and TDN regression analysis, in addition to Assawoman #4 as indicated above. Studentized residuals of greater than ±2 can be considered as potential outliers (Hair et al., 1998). Regression analysis results that include the outlier Little Mosquito-R Creek are provided in Fig. 7 and Tables 4 and 5. Annual FW concentrations of TDN and NO_3^- were positively related to % agricultural land cover and negatively related to % forested land cover, which was as expected given the negative correlation between these land uses (Fig. 7A, 7B; Table 4, single regressions #1 and 2). The TDN regression relationships were mainly driven by NO_3^- concentrations, as opposed to NH_4^+ or DON, because NO_3^- was the dominant N species present (Table 2); therefore, only NO_3^- regressions are shown in Fig. 7. In contrast to TDN and NO_3^-, FW PO_4^{3-} concentrations were not significantly related to % agricultural or forested land cover. There were no significant relationships observed between annual stream FW TDN or PO_4^{3-} concentrations and % developed lands, nor were there significant relationships between FW DOC and any of the land covers.

Table 2. Annual base flow-weighted concentration for NO_3^-, NO_2^-, NH_4^+, dissolved organic nitrogen (DON), total dissolved nitrogen (TDN), PO_4^{3-}, and dissolved organic nitrogen (DOC).†

Stream	Base flow-weighted mean concentration					
	NO_3^-	NH_4^+	DON	TDN	PO_4^{3-}	DOC
	μmol L^{-1}					
Little Mosquito-R	321.3 ± 35.1‡	1.4 ± 0.2	4.5 ± 1.6	327.2 ± 36.1	0.27 ± 0.04	307.5 ± 24.4
Little Mosquito-L	84.0 ± 20.4	4.5 ± 0.8	38.9 ± 16.1	127.8 ± 36.3	0.58 ± 0.11	530.4 ± 118.5
Assawoman #3	219.7 ± 14.5	1.1 ± 0.1	9.0 ± 3.2	229.8 ± 14.5	0.72 ± 0.03	267.9 ± 10.8
Assawoman #4	566.2 ± 158.4	16.8 ± 12.6	52.9 ± 31.9	641.0 ± 136.4	5.31 ± 0.95	657.2 ± 64.4
Gargatha	185.3 ± 14.3	1.8 ± 0.3	21.3 ± 6.0	208.6 ± 19.2	0.96 ± 0.04	337.2 ± 51.1
Nickawampus	200.8 ± 11.3	4.2 ± 0.9	2.5 ± 0.6	208.1 ± 12.1	0.23 ± 0.03	220.7 ± 16.8
Machipongo	65.9 ± 6.4	2.7 ± 0.6	8.0 ± 1.2	76.7 ± 7.8	0.23 ± 0.08	222.2 ± 29.7
Partings	118.8 ± 10.3	2.1 ± 0.4	6.5 ± 1.1	127.6 ± 10.3	0.24 ± 0.08	302.6 ± 46.1
Greens	116.9 ± 6.8	1.8 ± 0.2	2.0 ± 1.0	120.7 ± 7.0	0.30 ± 0.14	242.3 ± 17.1
Phillips	95.8 ± 23.2	5.0 ± 1.6	8.0 ± 3.4	108.9 ± 25.1	0.21 ± 0.10	251.1 ± 60.7
Mill	2.6 ± 0.5	5.1 ± 1.4	15.0 ± 4.9	22.7 ± 6.3	0.39 ± 0.18	491.0 ± 147.4
Holt-R	224.7 ± 26.5	1.2 ± 0.2	3.7 ± 2.4	229.7 ± 27.7	0.21 ± 0.06	336.7 ± 90.5
Holt-L	104.0 ± 12.7	2.3 ± 0.6	19.0 ± 4.8	125.0 ± 17.1	0.37 ± 0.09	377.7 ± 93.4
Taylor	76.6 ± 4.7	4.7 ± 0.6	9.5 ± 1.5	91.1 ± 5.9	0.61 ± 0.10	357.6 ± 59.3

† 100 μmol L^{-1} N = 1.4 mg N L^{-1}; 100 μmol L^{-1} P = 3.0 mg P L^{-1}; 100 μmol L^{-1} C = 1.2 mg C L^{-1}.

‡ Mean ± SE.

Table 3. Annual base flow yields for NO_3^-, NO_2^-, NH_4^+, dissolved organic nitrogen (DON), total dissolved nitrogen (TDN), PO_4^{3-}, and dissolved organic nitrogen (DOC).

Stream	Annual base flow yields					
	NO_3^-	NH_4^+	DON	TDN	PO_4^{3-}	DOC
	kg ha⁻¹ yr⁻¹					
Little Mosquito-R	12.63 ± 0.98†	0.05 ± 0.01	0.18 ± 0.05	12.87 ± 1.00	0.023 ± 0.002	10.36 ± 0.58
Little Mosquito-L	0.17 ± 0.03	0.01 ± <0.01	0.08 ± 0.02	0.26 ± 0.05	0.002 ± <0.001	0.91 ± 0.14
Assawoman #3	5.61 ± 0.26	0.03 ± <0.01	0.23 ± 0.06	5.87 ± 0.26	0.039 ± 0.001	5.86 ± 0.17
Assawoman #4	4.20 ± 0.83	0.12 ± 0.07	0.39 ± 0.17	4.76 ± 0.72	0.084 ± 0.011	4.18 ± 0.29
Gargatha	4.85 ± 0.26	0.05 ± 0.00	0.56 ± 0.11	5.46 ± 0.36	0.054 ± 0.002	7.56 ± 0.81
Nickawampus	8.86 ± 0.35	0.18 ± 0.03	0.11 ± 0.02	9.18 ± 0.38	0.022 ± 0.002	8.35 ± 0.45
Machipongo	0.42 ± 0.03	0.02 ± <0.01	0.05 ± 0.01	0.48 ± 0.03	0.003 ± 0.001	1.20 ± 0.11
Partings	2.77 ± 0.17	0.05 ± 0.01	0.15 ± 0.02	2.98 ± 0.17	0.012 ± 0.003	6.06 ± 0.65
Greens	2.18 ± 0.09	0.03 ± <0.01	0.04 ± 0.01	2.26 ± 0.09	0.012 ± 0.004	3.88 ± 0.19
Phillips	1.43 ± 0.24	0.08 ± 0.02	0.12 ± 0.04	1.62 ± 0.26	0.007 ± 0.002	3.21 ± 0.55
Mill	0.01 ± 0.00	0.03 ± 0.01	0.08 ± 0.02	0.13 ± 0.03	0.005 ± 0.001	2.36 ± 0.50
Holt-R	4.56 ± 0.38	0.02 ± 0.00	0.07 ± 0.03	4.66 ± 0.40	0.009 ± 0.002	5.85 ± 1.11
Holt-L	2.10 ± 0.18	0.05 ± 0.01	0.38 ± 0.07	2.53 ± 0.24	0.016 ± 0.003	6.54 ± 1.14
Taylor	2.38 ± 0.10	0.15 ± 0.01	0.30 ± 0.03	2.83 ± 0.13	0.041 ± 0.005	9.53 ± 1.12

† Mean ± SE.

Annual FW TDN, driven mainly by concentrations of NO_3^-, was positively related with % very poorly drained soil (Fig. 7C; Table 4, single regression #3). No significant relationships were observed between FW TDN, NO_3^-, NH_4^+, and DON and poorly drained or well drained soils. Similarly, DOC was not related to any soil types. In contrast, FW PO_4^{3-} was weakly and negatively related to poorly drained soils (Fig. 7D; $r^2 = 0.28$; $p = 0.062$) but not to very poorly or well drained soils. Multiple regression analysis showed that % agricultural land cover and very poorly drained soil together accounted for 72% of the variability of FW TDN and 73% of the variability of FW NO_3^-(Table 4, multiple regressions #4 and 6). Forested land cover and very poorly drained soils together explained 71 and 73% of the variability of FW TDN and NO_3^-, respectively (Table 4, multiple regressions #5 and 7).

As observed for flow-weighted concentrations in single regressions, TDN and NO_3^- yields were negatively related to % forested land cover, positively related to % very poorly drained soils (Table 5, single regressions # 1, 4, 5 and 8), and weakly but positively related to % agricultural land cover (Table 5, single regressions #2 and 6). Significant positive relationships were also found between TDN and NO_3^- yields and % developed land cover (Table 5, single regressions #3 and 7). Ammonium, DON, and DOC yields were not significantly related to any land cover or soil types. As with concentration, PO_4^{3-} yields were negatively related to % poorly drained soils ($r^2 = 0.53$; $p = 0.005$) but were not related to other soil types or land covers. Multiple regression analysis showed that forested or agricultural land covers along with % developed land covers and % very poorly drained soils accounted for 91 and 92% of the variability of TDN and NO_3^- yields, respectively (Table 5, multiple regressions #9–12).

When the outlier Little Mosquito-R Creek was included in the regressions of FW NO_3^- and TDN concentrations and

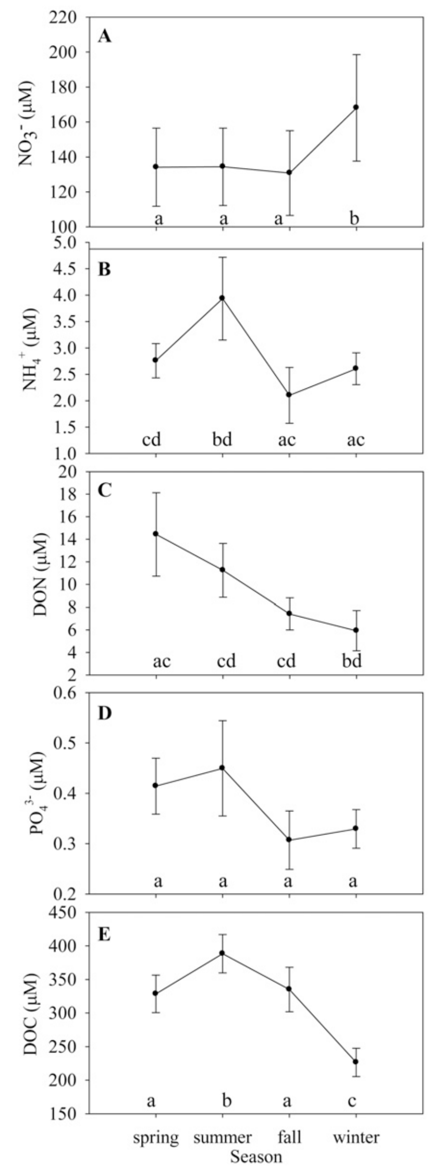

Fig. 6 (right). Seasonal mean base flow. (A) NO_3^-, (B) NH_4^+, (C) dissolved organic nitrogen (DON), (D) PO_4^{3-}, and (E) dissolved organic carbon (DOC) concentrations (±SE; μmol L⁻¹) ($n = 13$; no Assawoman #4). Different letters at the bottom of each figure denote significantly different seasonal mean values ($n = 13$; Tukey's test, $p < 0.05$).

Table 4. Single and multiple regressions for annual base flow-weighted total dissolved nitrogen (TDN) and NO_3^- concentrations in 12 streams (excluding Assawoman #4 and Little Mosquito-R Creeks), with watershed characteristics of land cover and soil drainage class as independent factors. Regression analysis results including the identified outlier Little Mosquito-R Creek is presented parenthetically. Single regressions for flow-weighted NO_3^- and PO_4^{3-} concentrations are presented in Fig. 7.

Regression no.	Dependent variable	r^2	*p* Value	Intercept	Coefficient for independent variable FOR†	AGR	VPD
	μmol L^{-1}						
Single regressions							
1	TDN	0.43 (0.11)	0.02 (0.27)	−21.20 (53.5)	–‡	2.97** (1.61)	–
2	TDN	0.54 (0.12)	0.007 (0.24)	278.84** (238.39**)	−3.26** (−1.92)	–	–
3	TDN	0.51 (0.34)	0.009 (0.04)	95.37** (106.19**)	–	–	9.99** (10.63*)
Multiple regressions							
4	TDN	0.72 (0.37)	0.003 (0.10)	−37.08 (56.06)	–	2.30* (1.02)	8.28* (9.69***)
5	TDN	0.73 (0.35)	0.003 (0.11)	199.97** (139.30)	−2.48* (−0.66)	–	6.85* (9.70***)
6	NO_3^-	0.73 (0.38)	0.003 (0.10)	−13.30 (35.78)	–	2.18* (1.09)	7.88* (10.19***)
7	NO_3^-	0.71 (0.36)	0.004 (0.11)	207.41** (128.00)	−2.28* (−0.77)	–	6.63* (10.10***)

† AGR, % agriculture; FOR, % forest; VPD, % very poorly drained.

‡ Independent variable not included in regression. Symbol after value indicates p value for testing significance of regression intercept and coefficients (* ≤0.05, ** ≤0.01, *** ≤0.1, none >0.1).

Table 5. Single and multiple regressions for base flow total dissolved nitrogen (TDN) and NO_3^- yields in 12 streams (excluding Assawoman #4 and Little Mosquito-R Creeks), with watershed characteristics of land cover and soil drainage class as independent factors. Regression analysis results including the identified outlier Little Mosquito-R Creek is presented parenthetically.

Regression no.	Dependent variable	r^2	*p* Value	Intercept	Coefficient for independent variable FOR†	AGR	DEV	VPD
	kg N ha^{-1} yr^{-1}							
Single regressions								
1	TDN	0.53 (0.07)	0.008 (0.39)	8.82** (6.83***)	−0.13** (−0.07)	–‡	–	–
2	TDN	0.30 (0.04)	0.07 (0.54)	−2.31 (1.33)	–	0.10*** (0.05)	–	–
3	TDN	0.40 (0.08)	0.03 (0.35)	1.96* (3.22*)	–	–	0.40* (0.25)	–
4	TDN	0.72 (0.40)	0.0005 (0.02)	1.02 (1.58)	–	–	–	0.49** (0.52*)
5	NO_3^-	0.52 (0.06)	0.008 (0.41)	8.37** (6.39***)	−0.13** (−0.06)	–	–	–
6	NO_3^-	0.29 (0.03)	0.07 (0.57)	−2.31 (1.31)	–	0.10*** (0.05)	–	–
7	NO_3^-	0.41 (0.08)	0.03 (0.36)	1.74* (3.00*)	–	–	0.39* (0.24)	–
8	NO_3^-	0.74 (0.39)	0.0003 (0.02)	0.81 (1.37)	–	–	–	0.48** (0.51*)
Multiple regressions								
9	TDN	0.91 (0.40)	0.0001 (0.19)	4.84** (1.53)	−0.08** (0.002)	–	0.17*** (−0.06)	0.28** (0.55***)
10	TDN	0.91 (0.40)	0.0001 (0.19)	−3.23* (1.70)	–	0.08** (−0.002)	0.26* (−0.06)	0.28** (0.55***)
11	NO_3^-	0.92 (0.40)	<0.0001 (0.19)	4.39** (1.12)	−0.08** (0.006)	–	0.17* (−0.06)	0.28** (0.55***)
12	NO_3^-	0.92 (0.40)	<0.0001 (0.19)	−3.19* (1.70)	–	0.08** (0.006)	0.25* (−0.07)	0.28** (0.55***)

† AGR, % agriculture; DEV, % developed; FOR, % forest; VPD, % very poorly drained.

‡ Independent variable not included in regression. Symbol after value indicates p value for testing significance of regression intercept and coefficients (* ≤0.05, ** ≤0.01, *** ≤0.1, none >0.1).

yields with the various land covers, they were not significant, although they demonstrated trends similar to those observed when the site was excluded (Tables 4 and 5). Little Mosquito-R Creek discharged much higher amounts of TDN and NO_3^- than streams with similar percentages of forest cover, as well as streams with predominantly agricultural land cover in their watersheds. The unusually high TDN and NO_3^- concentrations and yields might suggest that its watershed received greater N inputs due to different agricultural activities, that watershed boundaries (based on surface topography) did not incorporate all contributing areas, or that particular ecosystem (e.g., riparian buffer) functions responsible for N reduction were less efficient or bypassed. Little Mosquito-R Creek represented the most northern watershed studied and was located in a region with concentrated poultry farming and processing.

Discussion

Base Flow Discharge Rates

This study occurred during a significant drought that persisted from April 2001 to November 2002 and resulted in lower-than-average water table elevations and disruption of a more typical seasonal ground water recharge cycle (Fig. 2). Therefore, reported base flow discharge rates are expected to be lower than during more typical, average precipitation years with greater recharge of the surficial aquifer. Observed normalized base flow discharge rates in this study, ranging from 1.4 to 31.5 cm yr^{-1} (mean, 14.5 cm yr^{-1}; SD, 9.0), were lower than total (surface water runoff and base flow) discharge rates of 11 to 48 cm yr^{-1} (mean, 25.7 cm yr^{-1}; SD, 10.5) from 17 Coastal Plain, MD, and DE watersheds located in the northern Chesapeake Bay region (Jordan et al., 1997b). When these total discharge rates were adjusted with base flow indices for each of the streams, as described by Jordan et al. (1997a), base flow discharges were comparable to those reported in this study (range, 4.5–24.4 cm yr^{-1}; mean, 13.1 cm yr^{-1}; SD, 6.7). The 1-yr study by Jordan et al. (1997b) was also conducted during a period of lower-than-average long-term precipitation (95–106 cm versus 113 cm), when base flow would be expected to represent a larger fraction of total stream flow.

Nutrient Species

Nitrate, comprising 66 to 98% of the TDN, was negatively correlated to NH_4^+ concentrations. These results were expected because oxic conditions, commonly observed in streams and shallow upland ground water, support nitrification along the ground water flow path or within streams (Reay et al., 1992; Hamilton et al., 1993). Peterson et al. (2001) reported that assimilation and nitrification removed or transformed, respectively, 70 to 80% and 20 to 30% of NH_4^+ in 12 headwater streams throughout the USA. Mill Creek differed from the other streams in this study in that DON and NH_4^+ (63 and 22% of TDN, respectively) were the predominant N species present, perhaps due to the high % forest cover (67%) in its watershed and low stream flow. A large fraction of N input to streams with forested watersheds is frequently OM (particulate or dissolved) derived from forest production (Triska et al., 1984). Respiration of OM would generate NH_4^+ and reduce dissolved oxygen, potentially depressing nitrification and supporting dissimilatory NO_3^- reduction to NH_4^+ (Tobias et al., 2001).

The low dissolved PO_4^{3-} concentrations observed were most likely due to the binding of phosphorus (P) to particulates under oxic conditions (Wallbridge and Struthers, 1993). Jordan et al. (1997b) observed that total P concentrations in stream flow were correlated with particulate matter concentrations. The annual FW DIN:DIP ratios for the streams in this study ranged from 20 to 1183, indicating a strong potential for P limitation of primary production during base flow conditions. High DIN:DIP ratios are commonly found in Coastal Plain streams (TIN:TIP range, 51–450; Jordan et al., 1997b) and ground water (DIN:DIP range, 106–1092; Reay et al., 1992).

The positive correlations between DOC and DON concentrations may indicate that they were derived from similar in-stream sources, including exudation from benthic algae (periphyton), microbial degradation of particulate OM and leaf leachate, and leachates of riparian forest production in the watershed (Mulholland, 1992; Kaplan and Bott, 1982).

Seasonal Variability of Nutrient Concentrations

Seasonal variations in mean stream NO_3^- and NH_4^+ concentrations result in large part from processing by photoautotrophs and microbial communities in response to temperature, light, and substrate availability along ground water flow paths and during stream flow. Nitrate uptake in ground water flowing through the riparian forest zone is generally highest during the plant growing season, which begins in spring. In the winter, riparian forest removal of NO_3^- from ground water is inefficient (Correll et al., 1992), whereas soil microbial activity (i.e., denitrification, mineralization) in riparian forest and streambed is reduced due to low temperatures (Willems et al.,

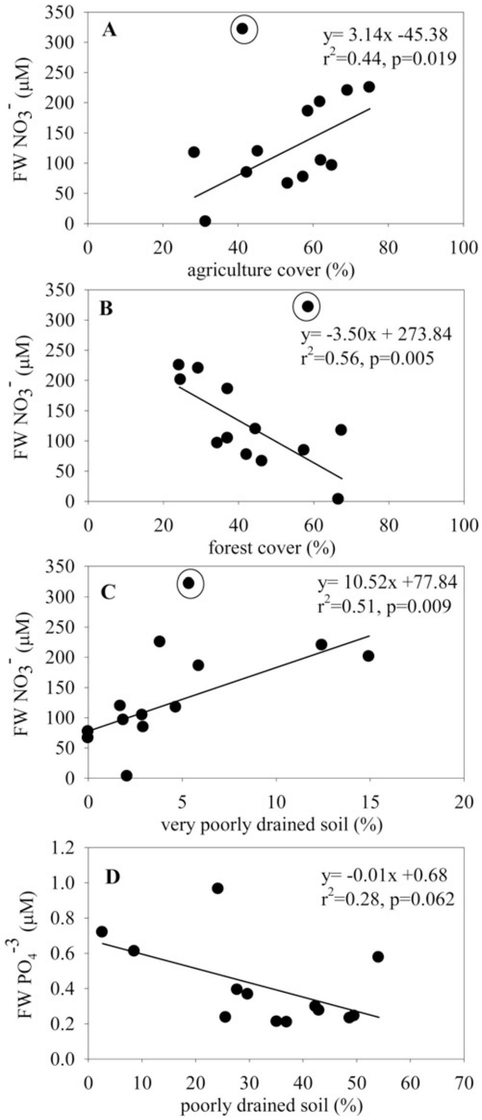

Fig. 7. Linear regressions of annual base flow-weighted (FW) NO_3^- concentration (µmol L^{-1}) with (A) percent agricultural land cover, (B) percent forested land cover, and (C) percent very poorly drained soil for 12 streams. Little Mosquito-Right Branch Creek was identified as an outlier (circled) and was not included in the regression analysis. If the outlier was included in the three FW NO_3^- regressions, the r^2 and p values for them are as follows: % agricultural: $r^2 = 0.11$, $p = 0.26$; % forested: $r^2 = 0.13$, $p = 0.23$; and % very poorly drained: $r^2 = 0.34$, $p = 0.04$. (D) Linear regression of annual FW PO_4^{3-} concentration (µmol L^{-1}) with percent poorly drained soil for 13 streams.

1997). In summer, higher NH_4^+ concentrations likely result from lower dissolved oxygen levels in streams and ground water, which reduce nitrification and increase mineralization rates (Mulholland, 1992). Mineralization and low dissolved oxygen may have contributed to the generally (although not significantly) higher PO_4^{3-} concentrations observed during the summer relative to fall and winter. Ammonia volatilization from soil, fertilizer, and animal waste and subsequent deposition are other potential sources of NH_4^+, which peak in spring/early summer due to warmer weather and timing of fertilizer application (Russell et al., 1998).

Higher temperatures and light availability during spring and summer can also increase DOC and DON concentrations due to greater in-stream activity of benthic algae and microbial communities. This seasonal pattern has been observed in other streams and headwater ground water seeps (Kaplan et al., 1980). Kaplan and Bott (1982) observed that net algal DOC excretion provided 20% of total DOC export from the watershed and that DOC concentrations in base flow in a Piedmont stream in Pennsylvania increased by as much as 40% above the daily minimum during the spring. In the fall, rapid leaching of leaf litter is a source of dissolved OM in streams, accounting for about 30% of daily DOC export (Meyer et al., 1998) and likely contributed to the relatively high fall DOC concentrations measured in our streams.

Relationships between Annual Base Flow Flow-weighted Mean Nutrient Concentrations and Yields with Watershed Characteristics

Because base flow is derived from ground water, our results clearly demonstrated that land cover and soil type have an impact on ground water NO_3^- concentrations. The negative relationship observed between forested land cover and NO_3^- concentrations and yields indicated that forested systems removed and/or sequestered NO_3^- from ground water before discharge to streams or that in watersheds with greater % forest cover, there were fewer agricultural fields and, thus, lower fertilizer N inputs. Although this study did not find a significant relationship, forested watersheds also tend to have lower water discharge rates due to greater evapotranspiration (Correll et al., 1992), which would lead to lower NO_3^- yields. Streams in watersheds with greater agricultural land cover also had higher NO_3^- concentrations and yields, likely due to nutrient inputs from fertilizer, manure, and crop N fixation. Many studies have shown that ground water NO_3^- concentrations are low under forests and elevated under agricultural land (e.g., Reay et al., 1991; Hamilton et al., 1993). Our results also indicated that developed land cover in watersheds contributed to higher base flow NO_3^- yields, which may be attributed to septic systems found in residential areas. Septic system effluent is composed predominantly of NH_4^+ (>99%), which may be nitrified to NO_3^- under oxic conditions (Reay, 2004). Valiela et al. (1992) observed that NO_3^- concentrations in ground water were significantly related to building density, a proxy for septic tank density.

We expected that watersheds with higher % poorly or very poorly drained soils would have lower NO_3^- because these soils are frequently saturated and anoxic and have high organic content, which support higher rates of denitrification. Low NO_3^- concentrations generally found under poorly drained, riparian forests have often been attributed to denitrification. However, we found higher NO_3^- concentrations and yields in watersheds with higher % very poorly drained soil (Fig. 7C). There are three possible explanations for this observed relationship. First, drought conditions may have lowered the water table, causing soils classified as very poorly drained to become unsaturated and more oxic, allowing for increased mineralization and subsequent nitrification and correspondingly higher NO_3^- concentrations. Magill et al. (2000) observed during drought conditions that a pine tree stand had increased rates of N mineralization, nitrification, and NO_3^- leaching from the soil relative to normal rain periods. Walling and Foster (1978) found that NO_3^- concentrations in river flow increased substantially during and after a drought (up to 45 times higher than previous years). They speculated that drying and rewetting of soil from scattered showers increased nitrification and mineralization rates, allowing accumulation of NO_3^-. Second, water table elevations may have been lowered below an organic-rich soil horizon to a substratum characterized by coarser textured sediments and lower OM content, thereby impacting processes that remove and/or transform N. Third, there may be autocorrelation between very poorly drained soils and the presence of other N sources. Streams located in Accomack County (Machipongo to Little Mosquito Creek-Right branch; see Fig. 1), where concentrated poultry farming is allowed, have greater proportions of very poorly drained soils (mean, 7.6%) compared with streams in Northampton County (mean, 2.4%) (Table 1). Poultry waste applied in excess of N crop demand, may have leached into ground water.

The low dissolved oxygen usually found in poorly drained soils generally results in release of PO_4^{3-} adsorbed to iron oxides. Higher dissolved PO_4^{3-} concentrations have been found in ground water under riparian forests with low oxygen levels and reducing conditions (Reay et al., 1991; Phillips and Bachman, 1996). Unexpectedly in this study, PO_4^{3-} concentrations and yields demonstrated negative relationships with % poorly drained soils (Fig. 7D). We suggest that due to the low water table caused by the drought, poorly drained soils might have become unsaturated and increasingly oxic, thereby promoting decreased PO_4^{3-} concentrations and yields.

The lack of significant relationships between NO_3^- and % poorly drained soils, as well as between PO_4^{3-} and % very poorly drained soils, may be due to the relatively low sample size in this study. In addition, there is likely some uncertainty and variability of the USDA mapping of soil types and drainage classifications and of the delineated watershed boundaries. Because watershed delineation was based on surface topography, there may be uncertainty in the watersheds' true ground water recharge area and boundaries.

Comparison of Base Flow Nutrient Yields from the Virginia Eastern Shore Watersheds to Watersheds in Chesapeake Bay

Reported annual TDN and NO_3^- yields from predominantly forested and agricultural watersheds in the VaES, measured during a low precipitation period (84.5 cm), were generally comparable to estimates for watersheds in the DE and MD portions of the Coastal Plain and Piedmont regions measured during higher precipitation years (108–113 cm) (Table 6). We would have expected the base flow dissolved N yields measured in this study to be lower than N yields observed in the DE and MD studies because their estimates were based on total stream flow (i.e., base flow and storm water runoff) and total nutrient composition, which included dissolved

Table 6. Comparison of base flow nutrient yields in VA Eastern Shore watersheds (Outer Coastal Plain region) to total nutrient yields in upper Delmarva Peninsula and Chesapeake Bay watersheds (Piedmont, Inner and Outer Coastal Plain regions). Adapted from Correll et al. (1999a, 1999b, 2001).

Watershed type, region, and state	% land cover	Stream flow†	Nutrient comp‡	Precip.	Yield: Total N	Yield: NO_3^-	Yield: NH_4^+	Yield: ON§	Yield: PO_4^{3-}	Yield: OC	Reference¶
				cm	kg ha^{-1} yr^{-1}						
Forested											
Piedmont, MD#	98	total	total	113	4.8	3.5	0.20	1.1	0.09	20.5	(A)
Coastal Plain, MD and DE#	91	total	total	113	1.3	0.06	0.23	1.0	0.009	16.4	(B)
Inner Coastal Plain, Rhode River, MD††	98	total	total	108	1.8	0.14	0.16	1.5	0.19	26.6	(C)
Inner Coastal Plain, Rhode River, MD‡‡	98	total	total	64.4	0.08	0.01	0.02	0.06	0.009	1.5	(C)
Inner Coastal Plain, Rhode River, MD‡‡	98	total	total	86.2	0.34	0.04	0.05	0.24	0.036	5.6	(C)
Outer Coastal Plain, VA—Mill Creek§§	67	base flow	dissolved	84.5	0.13 (0.08–0.18)¶¶	0.01 (0.01–0.02)	0.03 (0.02–0.04)	0.08 (0.05–0.12)	0.005 (0.002–0.008)	2.4 (1.4–3.4)	this study
Outer Coastal Plain, VA—Greens Creek§§	68	base flow	dissolved	84.5	2.3 (2.1–2.4)	2.2 (2.0–2.4)	0.03 (0.03–0.04)	0.04 (0.01–0.06)	0.012 (0.004–0.020)	3.9 (3.5–4.3)	this study
Agricultural											
Piedmont, MD#	62	total	total	113	16.2	14.1	0.30	1.8	0.16	15.3	(A)
Coastal Plain, MD and DE#	58	total	total	113	11.2	8.0	0.69	2.6	0.34	33.3	(B)
Inner Coastal Plain, Rhode River, MD††	64	total	total	108	7.3	3.8	0.51	3.0	1.40	35.3	(C)
Inner Coastal Plain, Rhode River, MD‡‡	64	total	total	64.4	0.94	0.65	0.08	0.19	0.028	2.4	(C)
Inner Coastal Plain, Rhode River, MD‡‡	64	total	total	86.2	2.6	1.5	0.20	0.72	0.18	8.6	(C)
Outer Coastal Plain, VA—Assawoman no. 3§§	69	base flow	dissolved	84.5	5.9 (5.4–6.4)	5.6 (5.1–6.1)	0.03 (0.02–0.03)	0.23 (0.12–0.34)	0.039 (0.037–0.041)	5.9 (5.5–6.2)	this study
Outer Coastal Plain, VA— Nickawampus§§	62	base flow	dissolved	84.5	9.2 (8.4–9.9)	8.9 (8.2–9.6)	0.18 (0.13–0.24)	0.11 (0.07–0.15)	0.022 (0.018–0.026)	8.4 (7.5–9.2)	this study
Outer Coastal Plain, VA—Phillips Creek§§	65	base flow	dissolved	84.5	1.6 (1.1–2.1)	1.4 (1.0–1.9)	0.08 (0.04–0.11)	0.12 (0.05–0.19)	0.007 (0.002–0.011)	3.2 (2.1–4.3)	this study
Outer Coastal Plain, VA—Holt-R Creek§§	75	base flow	dissolved	84.5	4.7 (3.9–5.4)	4.6 (3.8–5.3)	0.02 (0.02–0.03)	0.07 (0.01–0.14)	0.009 (0.005–0.013)	5.9 (3.7–8.0)	this study
Outer Coastal Plain, VA—Holt-L Creek§§	62	base flow	dissolved	84.5	2.5 (2.1–3.0)	2.1 (1.8–2.5)	0.05 (0.03–0.06)	0.38 (0.25–0.52)	0.016 (0.010–0.021)	6.5 (4.3–8.8)	this study

† Total stream flow consists of storm water runoff and base flow.

‡ Nutrient component for all yields. Total consists of dissolved and acid-extractable particulate nutrients.

§ OC, organic carbon; ON, organic nitrogen.

¶ (A) Jordan et al., 1997c; (B) Jordan et al., 1997b; (C) Correll et al., 1999a, 1999b, 2001.

Precipitation was long-term mean. Annual flow-weighted mean total nutrient concentrations from 1-yr study and long-term average water discharge rates (5–27 yr) were used to calculate yields. Watersheds were from inner, central, and outer Coastal Plain regions.

†† Mean precipitation and yields from 18-yr study.

‡‡ Loading rate values calculated from regression of nutrient yields versus precipitation at 1 and 2 SD below mean precipitation. Prediction for 644 mm precipitation was extrapolated beyond the lowest observed annual precipitation (824 mm) during study.

§§ Precipitation was average of eight precipitation stations on the Virginia Eastern Shore.

¶¶ For watersheds in this study, 95% confidence intervals are provided parenthetically.

and acid-extractable particulate nutrients (Correll et al., 1999a, 1999b, 2001). The similarity between our base flow estimates and the DE and MD total stream flow estimates during higher precipitation years suggests that base flow was a more important source of NO_3^- compared with storm water runoff. Jordan et al. (1997a) noted that NO_3^- concentrations increased as the proportion of base flow increased in streams of the Piedmont and Coastal Plain regions of the Chesapeake Bay. Bohlke and Denver (1995) found lower NO_3^- concentrations in storm flow samples taken during rain events than in base flow samples. In addition, our forested watersheds had lower percentages of forest than the other studies' forested watersheds, which could also lead to greater N inputs. In contrast to total N and NO_3^-, organic N (ON), organic C (OC), and P fluxes from our watersheds were closer to those in the DE and MD watersheds measured during lower precipitation years (64–87 cm). This may be explained by the often particulate nature of P, OC, and ON (P: 63–89%; OC and ON: 21–62%) (Jordan et al., 1997b) and by the lower concentrations of particulates likely to be found in streams during periods of low stream flow.

Prediction of Base Flow Total Dissolved Nitrogen Loading from Hog Island Bay Watersheds

Understanding and quantifying direct and indirect N sources is critical for proper management of water quality and associated eutrophication in coastal systems. Results of this study can be used to estimate base flow N loadings to coastal bays and lagoons of the VaES, such as HIB with 51.4% forested, 45.3% agricultural, and 3.3% developed land cover (Porter and Hayden, 2001). Predicted TDN yields from each of HIB's 16 watersheds, which were calculated using the multiple regression model that included percentages of agricultural and developed land covers and very poorly drained soil (Table 5, regression #10), ranged from 0.61 (95% prediction interval [PI], 0–3.05) to 5.73 (PI, 2.16–9.28) kg N ha^{-1} yr^{-1}. Estimated TDN loading from all HIB watersheds (total area, 9217 ha) was 28,170 (95% PI, 5290–53,840) kg N yr^{-1}, thereby yielding a base flow yield of 3.06 (95% PI, 0.57–5.84) kg N ha^{-1} yr^{-1}. The estimated TDN loading, based on the multiple regression using forested instead of agricultural land cover (Table 5, regression #9), produced a similar result (27,850 kg N yr^{-1}; 95% PI, 5260–53,870).

Conclusions

This study occurred during a significant drought, which likely affected base flow quantity and quality. Along with reductions in base flow discharge, one would anticipate increased contribution of base flow to total stream flow as well as greater influence of base flow on water chemistry. With a lower water table elevation, a greater proportion of older, NO_3^-–rich ground water from greater depths (Hamilton et al., 1993) may discharge to the stream, or ground water may bypass the riparian forest root zone (Speiran, 1996). In addition, we might expect less dilution of older, NO_3^-–rich ground water as a result of decreased recharge of water through the forested soil. Lastly, during low-flow drought conditions when throughput rates are low relative to biotic uptake, we might expect greater in-stream nutrient recycling and processing, which can affect nutrient species and concentrations. A multi-year study of the streams and increased sample size would help to assess relationships between nutrient concentrations and N yields with precipitation as well as effects of drought on N transformations in very poorly drained soils.

The multiple regression models developed in this study were used to estimate base flow N loadings to Hog Island Bay and can be applied to other bays and coastal lagoons on the VaES. Resource managers can use this information to assess the relative importance of base flow as an N source compared with other sources, such as surface water runoff and atmospheric deposition, and thus to prioritize their strategies to effectively reduce N inputs to coastal ecosystems.

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