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Export of nitrogen, phosphorus, and suspended solids from a southern New England watershed to Little Narragansett Bay

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Abstract. The Pawcatuck River watershed (764 km^2) is a mainly forested drainage basin with a low population density (80 people km^{-2}) that discharges to a shallow estuary, Little Narragansett Bay (RI and CT, USA). In order to quantify the nitrogen (N) and phosphorus (P) flux to the estuary, we measured all forms of nitrogen and phosphorus, as well as suspended solids at the mouth of the river above tidal influence, on more than 80 occasions over an annual cycle. The annual export of total nitrogen, total phosphorus, and total suspended solids amounted to 16.0×10^6 mol y^{-1}, 0.97×10^6 mol y^{-1}, and 1.4×10^6 kg y^{-1}, respectively. Nitrogen export was equally divided between dissolved inorganic (83% NO_3^-) and organic forms, with particulate nitrogen comprising 17% of the total flux. Phosphorus export was dominated by particulate forms (67%), with dissolved inorganic phosphate contributing 30% and dissolved organic phosphorus contributing 8% of the annual flux. Preliminary nutrient budgets for the Pawcatuck watershed suggest that only about 10% of the nitrogen and phosphorus inputs are exported from the system. Strong regressions between water discharge and TN enabled us to extrapolate the data collected during the relatively dry study period to a long term average discharge year. Under normal river discharge conditions, the N flux would be approximately 26.0×10^6 mol y^{-1} or about 20% of the nitrogen inputs to the watershed. This value is very close to the N flux predicted by a regression developed by others from a wide range of larger watersheds. The relatively large size of the Pawcatuck watershed relative to the estuary (9.6 km^2), makes Little Narragansett Bay one of the most intensively nitrogen loaded estuaries on the Atlantic coast in spite of the dominant forest cover of the watershed.

Introduction

Coastal watersheds are intimately connected with their downstream estuaries through riverine transport of anthropogenic pollutants and soil weathering products (Meybeck 1979, 1988; Howarth et al. 2002). For this reason, numerous efforts have been made to measure the flux of pollutants and other materials in a wide variety of rivers and streams at or near the point where they first encounter salt water (e.g., Nanaimo River, British Columbia, Canada, Naiman and Sibert 1978; Narragansett Bay, Rhode Island, United States, Nixon et al. 1995; Cantabrian Rivers, Spain, Prego and Vergara 1998; Atchafalaya River, Louisiana, United States, Lane et al. 2002, and numerous others). By quantifying the loss of materials from an upstream drainage basin we can simultaneously learn about some aspects of the biogeochemical cycles and nutrient budgets of watersheds and calculate the inputs of materials to coastal marine systems. These measurements provide a highly aggregated view of the net result of all the various sources, sinks, and transformations that are active in the watershed, including in-stream, riparian, and terrestrial components.

We had two major motivations for measuring the transport of nitrogen (N), phosphorus (P), and total suspended solids (TSS) from the Pawcatuck watershed. First, we wanted to examine nutrient dynamics in a predominantly forested watershed: (1) How do nutrient concentrations respond to river discharge? (2) What is the nutrient retention rate? and (3) How does this watershed compare with other forested watersheds? Second, we wanted to quantify inputs to Little Narragansett Bay, a small (9.6 km^2), shallow (mean depth 2 m) estuary at the eastern end of Long Island Sound, on the southern border between Rhode Island and Connecticut (USA). Little Narragansett Bay provides important habitat for birds, finfish, and shellfish. Once replete with eelgrass beds, this embayment now exhibits signs of nutrient enrichment, including loss of submerged aquatic vegetation, increased macroalgae growth, and increased frequency and duration of hypoxic and anoxic events (Desbonnet and Banister 1994; Jordan 1998). This is surprising considering the fact that the Pawcatuck watershed is the least developed in the state (>60% forest) and has a low population density (80 people km^{-2}).

We present here highly resolved annual cycles (12/6/01–11/30/02) of all forms of nitrogen, phosphorus, and TSS at the mouth of the Pawcatuck river in order to better understand the changes occurring in Little Narragansett Bay. Constituent concentrations were measured on more than 80 occasions and annual fluxes calculated by combining our measurements with water discharge measured by the United States Geological Survey (USGS) at the same site. These highly resolved cycles allow us to compare our measured N and P fluxes to those predicted by empirical relationships between simple features such as human population density and nutrient export (Peierls et al. 1991; Caraco and Cole 1999a) or between total anthropogenic nitrogen input to a watershed and nitrogen export (Howarth et al. 1996; Boyer et al. 2002; van Breemen et al. 2002). We are also able to compare N and P losses from this undeveloped watershed to the more developed urban watersheds in northern Rhode Island (Nixon et al. 1995) and to compare area specific nutrient loading rates between Little Narragansett Bay and the more urbanized Narragansett Bay as well as other well known estuaries in the northeast United States.

Methods

Site description

The Pawcatuck Watershed (797 km^2) is located predominantly in Rhode Island with a small portion extending into northeastern Connecticut. Two main drainage systems define this watershed. The Pawcatuck River (47 km) begins near Worden Pond on the eastern edge of the watershed and runs west, then south to Little Narragansett Bay. The Wood River (29 km) runs from north to south and joins the Pawcatuck River at Wood River Junction (Figure 1). A majority (70%) of the Pawcatuck drainage system is comprised of first and second order streams (Rosenblatt 2000) and approximately 63 bodies of freshwater account for just under 2% (15 km^2) of the watershed (Desbonnet 1999). Of the 797 km^2 of the Pawcatuck Watershed, 95% (764 km^2) drains to the river above our sampling site. For the remainder of the paper, when we discuss the watershed, we are referring to the 95% above our sampling site.

The southern border of the Pawcatuck watershed is a 30 m high glacial moraine formed over 16,000 years ago by the Laurentide ice sheet (Ehinger et al. 1978). This glacier redirected the surface water flow from a north–south orientation to the east–west position seen today (Desbonnet 1999). Soils are approximately 55% glacial till, 30% glacial outwash, and 10% organic and alluvial with the principal soil orders being Inceptisols, Histosols, and Entisols (Rosenblatt et al. 2001). Most of the drainage basin is flat (0.6% average slope), with the highest elevation (200 m) found in the northern reaches of the watershed. Such subtle terrain accounts for the slow moving surface waters necessary for the varying landscape of red maple swamps, Atlantic white cedar evergreen swamps, and freshwater marshes and bogs which characterize about 15% of the Pawcatuck watershed (Pawcatuck Watershed Partnership 1998). Most of the watershed remains forested, with mixed oak hardwoods, mainly red oak (*Quercus rubra*) and the softwood, eastern white pine (*Pinus strobus*). Agriculture accounts for less than 10% of the land within the Pawcatuck watershed and is dedicated primarily to turf production. Small farms in the area support some livestock, predominantly cattle and chickens (USDA 1997).

The human population of the Pawcatuck watershed is focused mainly in small town centers and suburban communities, with little commercial property and only two industrial point sources. We used the 2000 census information to calculate the population of the watershed by multiplying the area of each census block within the watershed by the population density of that block. The results suggest that approximately 60,000 people live in the watershed (80 people km^{-2}). This compares with the population density of 426 people km^{-2} in the much more developed Narragansett Bay watershed.

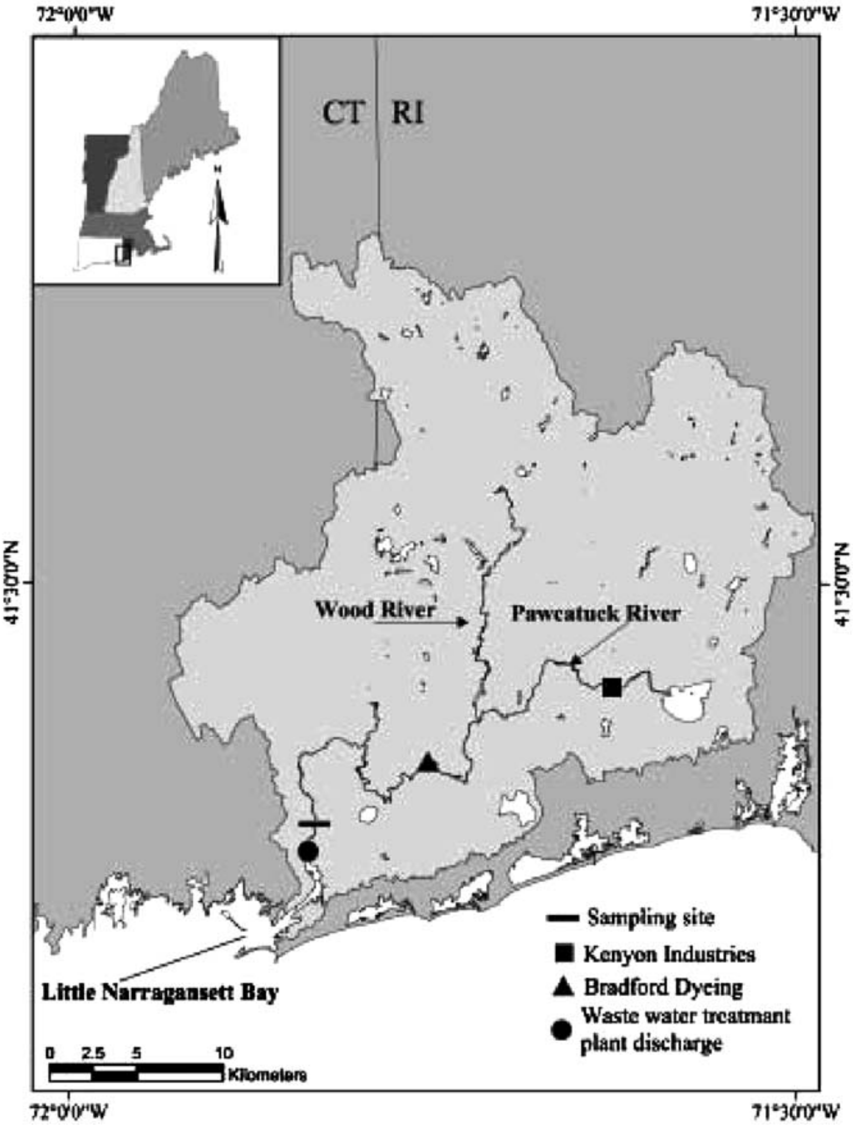

Figure 1. Location of the Pawcatuck watershed. The bar marks the water sampling site used in this study and the United states Geological survey water discharge gage (41°23′01″;71°50′01″) in Westerly, Rhode Island. Circles and squares represent point source discharge into the Pawcatuck River and Pawcatuck River estuary. Cartographic data were obtained from the Rhode Island Geographic Information systems (RIGIS).

Field sampling

We collected water samples at the Stillmanville Dam in Westerly, Rhode Island, where the Pawcatuck is still a free flowing river not influenced by the tide. There is also a long-term water discharge record at this site, where the United States Geological Survey (USGS) calculates discharge from stage height every 15 min. Water samples were collected for concentration measurements on 80 occasions over a wide range of water discharge values from December 6, 2001 through November 29, 2002 (Figure 2).

Polyethylene bottles (500 ml) that had been rinsed and leached with deionized water were used to collect water samples. Each bottle was rinsed with river water three times before the final sample was taken and stored (<3 h) on ice for processing in the laboratory. Dissolved total and inorganic nitrogen and phosphorus samples were filtered using a 60 ml polypropylene syringe and precombusted (400 °C for 4 h) glass fiber filters (Whatman GF/F 0.70 μm). The filtrate was captured in 60 ml acid washed and deionized water leached polyethylene bottles and stored at -15 °C until analysis. We used precombusted glass fiber filters (Whatman GF/F 0.70 μm) and acid washed and oven-dried glassware with a polyvinyl chloride manifold in the filtration process for particulate nitrogen (PN). PN samples were dried at 60 °C and stored in a dessicator until analysis. Particulate phosphorus samples (PP) were obtained by filtering 125 ml of river water using acid washed and oven dried glassware and glass fiber filters (Whatman GF/F 0.70 μm). These samples were frozen until analysis. TSS were collected as explained for particulate phosphorus. However, the volume of water filtered varied on each occasion (150–1100 ml) and, instead of being frozen, these samples were placed in a drying oven at 60 °C for 2 weeks or until dry weights could be taken.

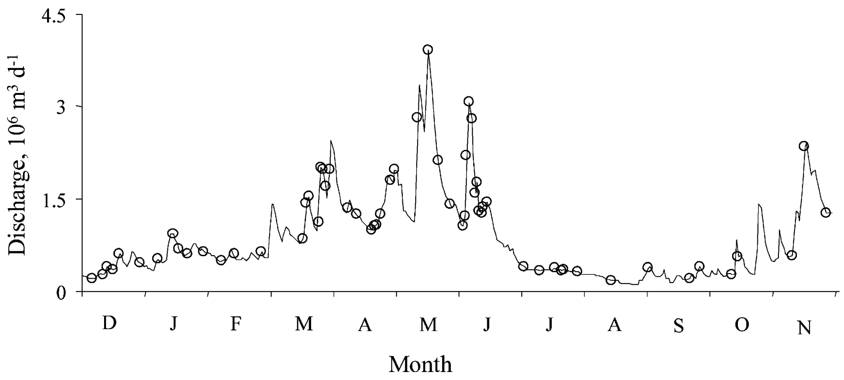

Figure 2. Mean daily water discharge for the study period (12/06/01–11/29/02) at Westerly, Rhode Island. Open circles represent days on which water samples were taken for analysis of all forms of nitrogen, phosphorus, and total suspended sediments. USGS flow data were obtained at 15 min intervals and averaged over 24 h periods.

Analytical methods

We used a Lachat Instrument QuikChem 8000 flow injection analyzer to determine concentrations of nitrite (NO_2^-), nitrate (NO_3^-), ammonium (NH_4^+), and dissolved inorganic phosphorus (PO_4^{-3}). Total dissolved nitrogen (TDN) and total dissolved phosphorus (TDP) were determined by persulfate digestion, while particulate phosphorus (PP) was determined by high temperature combustion followed by HCL extraction. Each was followed by determination of nitrate or phosphate on the extract (Table 1). Dissolved organic nitrogen and dissolved organic phosphorus were measured by subtracting the inorganic component (DIN or DIP) from the total dissolved portion (TDN or TDP). TN and TP results are the sum of the total dissolved and particulate components. TSS concentration was determined from the average of three dry weights. The TSS samples were re-weighed after combustion at 500 °C for 6 h to determine percent organic matter.

Data analysis

Instantaneous fluxes were determined by multiplying the individually measured concentrations by the corresponding USGS water discharge value taken from the closest 15 min interval reading. We then used Beale's ratio estimator (Beale 1962; Dolan et al. 1981) to calculate annual fluxes of each constituent measured for the 12 months between December 1, 2001 and November 30, 2002 (Fulweiler 2003). This estimator provides an unbiased, flow-weighted annual flux estimate for data that are skewed and/or not normally distributed (Richards and Holloway 1987; Richards 1999), two features that characterized this data set. Beale's ratio estimate is calculated by:

$$\tilde{\mu}_y = \mu_x \frac{m_y}{m_x}\left(\frac{1 + \frac{1}{n}\frac{S_{xy}}{m_x m_y}}{1 + \frac{1}{n}\frac{S_{x^2}}{m_{x^2}}}\right)$$

Table 1. Analytical methods used in study.

Parameter	Method reference	Detection limit (μM)
Ammonium	USEPA Methods 365.3 Grasshoff (1976)	0.07
Nitrite + Nitrate	USEPA Method 353.2 Grasshoff (1976)	0.02
Total Nitrogen	Valderrama (1981)	0.02
Particulate Nitrogen	Hauck (1982) Kirsten (1983)	< 0.03
Orthophosphote	USEPA Method 365.5 Grasshoff (1976)	0.01
Total Phosphorus	Valderrama (1981)	0.01
Particulte Phosphours	Solorozano and sharp (1980)	00.10

where S_{xy} is equal to:

$$S_{xy} = \frac{1}{(n-1)} \sum_{i=1}^{n} x_i y_i - n m_x m_y$$

and S_{x^2} is:

$$S_{x^2} = \frac{1}{(n-1)} \sum_{i=1}^{n} x_{i^2} - n m_{x^2}$$

The estimated annual flux is $\tilde{\mu}_y$, $\tilde{\mu}_x$ is mean daily discharge over the annual cycle, m_y is the mean daily loading for days on which concentrations were determined, m_x is the mean daily discharge for those days on which concentrations were determined, and n is equal to the number of days on which concentrations were determined. Individual measured flows and concentrations are represented by x_i and y_i, respectively (Dolan et al. 1981).

Preliminary inventory of watershed nutrient inputs

Human waste

Approximately 42,000 people in the watershed use individual household septic systems, with the remainder served by two wastewater treatment plants which discharge below our sampling site (Pawcatuck Watershed Partnership 1998). Nixon et al. (in prep.) determined the daily per capita N and P release rate based on raw sewage monitoring data from the two largest wastewater treatment facilities in RI over a 2 year period (2001–2003). The concentration of N and P in untreated sewage was multiplied by the volume of influent and divided by the number of people served to obtain an average release rate of 15 g N and 1.8 g P per person per day. We used these daily release rates and a septic tank removal rate of 20% to estimate the amount of N and P added to the watershed by septic tanks (Gold et al. 1990). The N and P accumulated in septic tanks is collected periodically and trucked to disposal plants which discharge outside of the study area.

Industrial point sources

Data available through the U.S. Environmental Protection Agency's NPDES program (National Pollutant Discharge Elimination System) show that effluents containing high levels of orthophosphate from two textile finishing plants are discharged into the Pawcatuck River above the sampling site. We were unable to obtain information on how much phosphate the two plants bring into the watershed. As a minimum estimate, we assumed the input was equal to the amount of DIP discharged to the river. We calculated the latter from the NPDES concentration and effluent discharge data extrapolated to an annual basis.

Fertilizer
The weight of nitrogen and phosphorus fertilizer (reported as total N and total P) sold in Rhode Island during 2001–2002, for both agricultural and non-agricultural use, is only available on a statewide basis (Stephen Volpe, personal communication, Agricultural Department, RIDEM 2003). As in the Pawcatuck watershed, most agriculture land in Rhode Island is dedicated to turf. We therefore divided the total fertilizer sales by the agricultural area of the state and applied the result to the area of agricultural land in the Pawcatuck watershed. Since the total sales include non-agricultural use, this may overestimate inputs to the watershed.

Livestock
The population of cattle, pigs, poultry, sheep, and horses was available for the four counties (Washington and Kent in Rhode Island and New London and Windham in CT) that are included in the watershed from the 1997 census of agriculture (USDA 1997). We assumed that the livestock were evenly distributed throughout each county and determined the amount of livestock in the watershed by multiplying the percentage of county in the watershed by the appropriate livestock population. We then multiplied the livestock population by the average N and P produced per animal per year to determine the total loading to the watershed (Stanley 1992). Unfortunately, we do not know the fate of this livestock waste nor do we know the contribution of domestic pets (cats and dogs) to the overall nutrient budget.

Atmospheric deposition
We estimated total N atmospheric deposition, including dry deposition and organic nitrogen, based on 3 years of measurements at nearby Avery Point, CT (Luo et al. 2002). Data for wet and dry phosphorus deposition rates are available from four sites throughout Connecticut (Yang et al. 1996). We used a 3 year average of data from Hammonasset State Park in Madison, CT, approximately 80 km from our sampling site.

Results and discussion

Seasonal cycles

River discharge
The 60 year mean daily discharge at this site is 1.46×10^6 m^3 d^{-1}, and ranges from 0.73×10^6 m^3 d^{-1} in 1981 to 4.06×10^6 m^3 d^{-1} in 1948. This study took place toward the end of a drought period in New England that was first identified in January 2002, after a fall and winter of below normal precipitation (NOAA 2002; Terebus 2002). Bulk precipitation was below the long-term average (1912–2002) in 2001 and during 4 months (January, February, July, and August) of the study period. In 2002, as the drought subsided, precipitation increased resulting

in an overall bulk precipitation for this study of 117 cm. This is similar to the 80 year mean of 118 cm. However, the mean daily discharge (0.83×10^6 m^3 d^{-1}) over the 12 month sampling period was only 60% of the annual long-term mean. The range of water discharge on days sampled during this study varied almost 40-fold, from 0.09×10^6 m^3 d^{-1} in August to 3.9×10^6 m^3 d^{-1} in May. Runoff for this study was 38 cm y^{-1} or about 32% of the bulk precipitation, also well below the 60 year mean (64 cm y^{-1}, or 50% of precipitation).

Nitrogen

Seasonal variations in concentrations differed for each form of dissolved inorganic nitrogen (DIN) (Figure 3a–c). Ammonium concentrations were

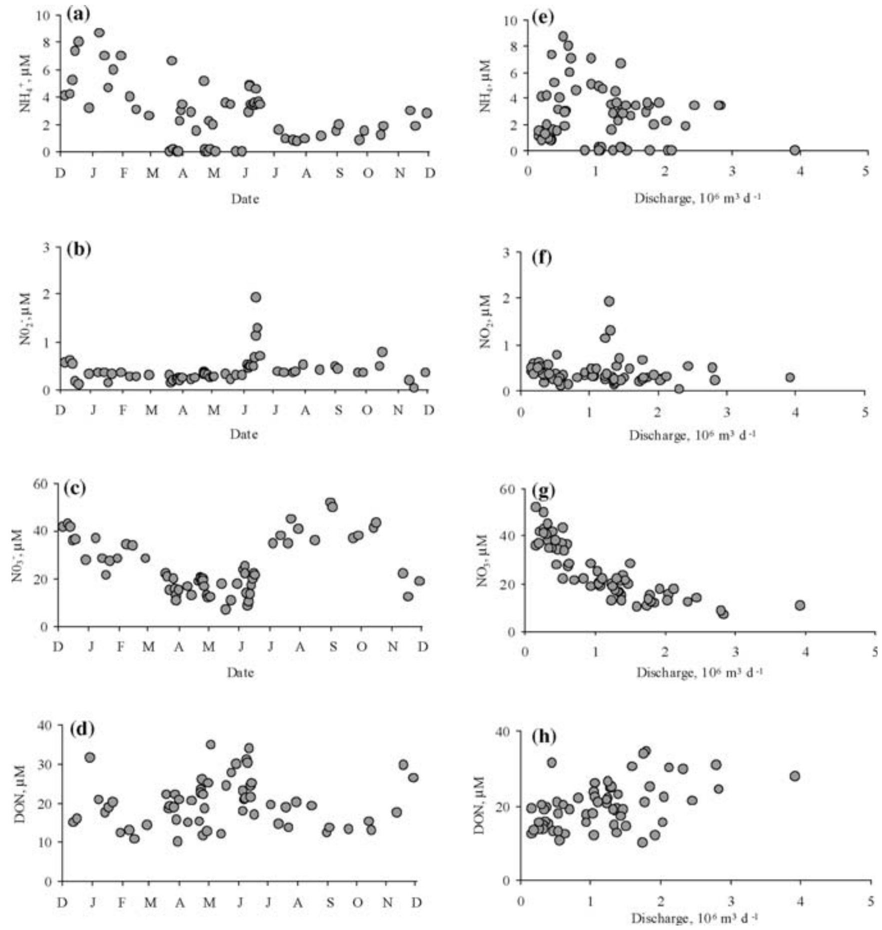

Figure 3. (a–h) Ammonium ($NH^+{}_4$), nitrate ($NO^-{}_2$), nitrate ($NO^-{}_3$) and dissolved organic nitrogen (DON) concentrations (μM) as a function of time and river discharge over the study period (12/6/01–11/29/02).

lower at the end of the study than at the beginning, perhaps reflecting an influence of the drought during the early months. In contrast to some other New England rivers (Campbell et al. 2000; Goodale et al. 2000), dissolved organic nitrogen concentrations showed considerable variability and ranged from 10 μM to just under 34 μM, with a mean of almost 20 μM (Figure 3d).

Ammonium and nitrite concentrations did not vary in a regular way with water discharge, while DON concentrations increased slightly (Figure 3e–h). Nitrate concentrations clearly decreased at increasing discharge, which might suggest that point sources within the watershed provide a significant amount of the DIN (Prego and Vergara 1998). However, there are no known point sources of nitrogen within the watershed. The apparent 'dilution' is not due to rainfall, since bulk precipitation in this area averages 46 μM of DIN, with higher concentrations during spring (Fraher 1991). We speculate that the uptake of DIN from groundwater by terrestrial vegetation is responsible for the seasonal decline in DIN concentrations in spring and summer, as it may be for dissolved silica (Fulweiler and Nixon 2005).

A majority (83%) of the nitrogen transported in the Pawcatuck River was in dissolved form (TDN). TDN composition was dominated by DIN at low water discharge and by DON at high water discharge (Figure 4a). As river discharge increased, the DIN:DON ratio decreased exponentially, and DIN and DON were negatively correlated throughout the study (Figure 4b–c). One explanation for this pattern is that low discharge increases the residence time of DON in the system, thus allowing increased mineralization of DON. During non-drought years, DON may comprise more of the total dissolved nitrogen exported from the Pawcatuck watershed. The bioavailability of DON, while not measured in the Pawcatuck watershed, may be important for contributing to productivity in downstream estuaries (Seitzinger and Sanders 1997; Seitzinger et al. 2002a; van Breeman 2002) Seitzinger et al. (2002a) found that DON draining a northeast hardwood forest was 50% bioavailable. If the DON in the Pawcatuck River is similar, the DON flux to Little Narragansett Bay might ultimately provide about half as much reactive N as the DIN flux.

Dissolved organic carbon (DOC) and particulate carbon (PC) concentrations were also measured in the Pawcatuck River and the results have been reported previously (Fulweiler et al. 2003). A weak positive correlation between DOC and DON exists and the annual integrated DOC:DON molar flux ratio was 24 (Figure 5). Goodale et al. (2000) report annual mean DOC:DON ratios ranging from 17 to 53 that they believe reflected land use history for 14 temperate New England forested watersheds. The Pawcatuck watershed has a mixed land use history and was extensively cleared for agriculture using a variety of methods until the mid-1800s (RIDEM 2002). However, the annual DOC:DON ratio of 24 for the Pawcatuck is considerably lower than the ratios for a mixed land use history found in Goodale et al. (2000).

Particulate nitrogen (PN) concentrations exhibited no seasonal trends, a weak correlation with discharge, and, with few exceptions, little variability over the year (Figure 6). The mean molar ratio of PC:PN was 8 and did not vary

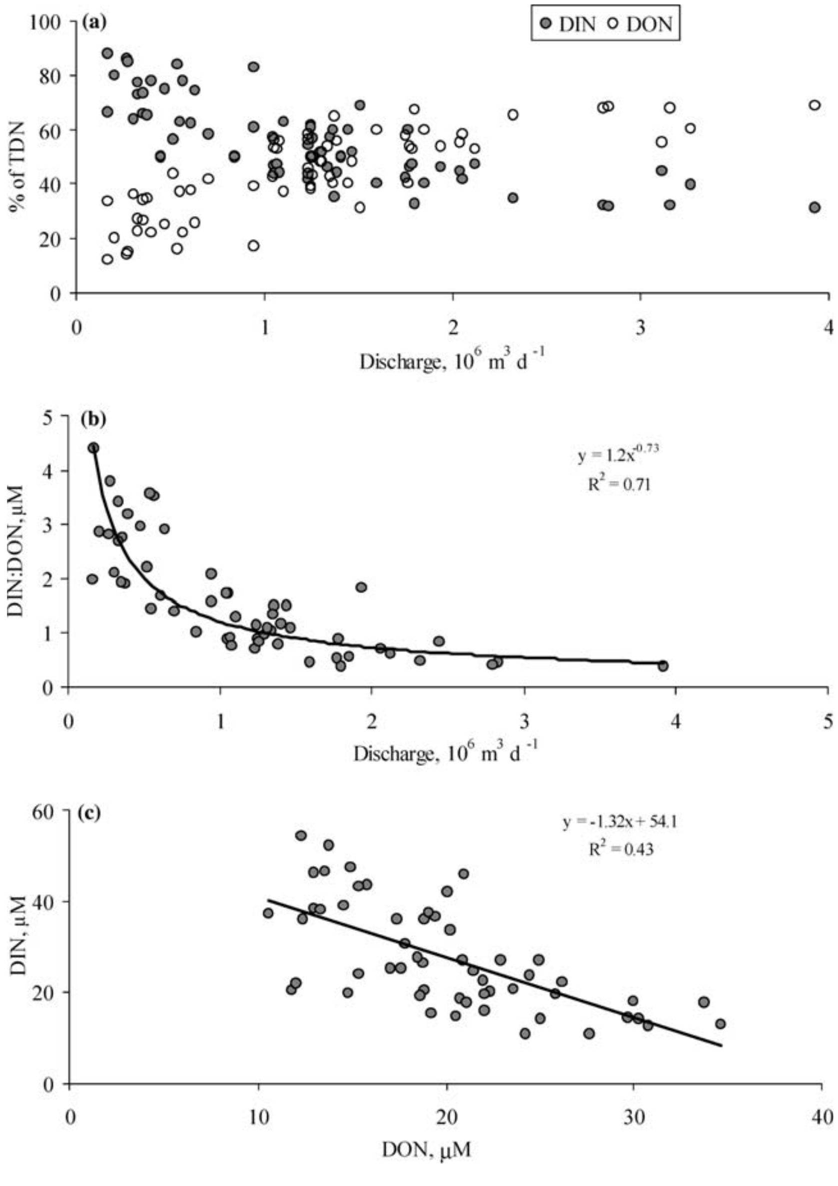

Figure 4. (a) Total dissolved nitrogen composition as a function of river discharge as measured at the mouth of the Pawcatuck river; (b) Molar DIN:DON as a function of water discharge; (c) DIN concentration (μM) as a function of DON concentration (μM) as measured at the mouth of the Pawcatuck River from 12/06/01–11/29/02.

seasonally or with water discharge. This suggests that the particulate organic matter had high nutritional value and may be an important food source within the Pawcatuck River. Elser et al. (2000) showed that gross growth efficiency for in stream grazers dropped from about 25% to 10% as food C:N ratio increased from 10 to 35.

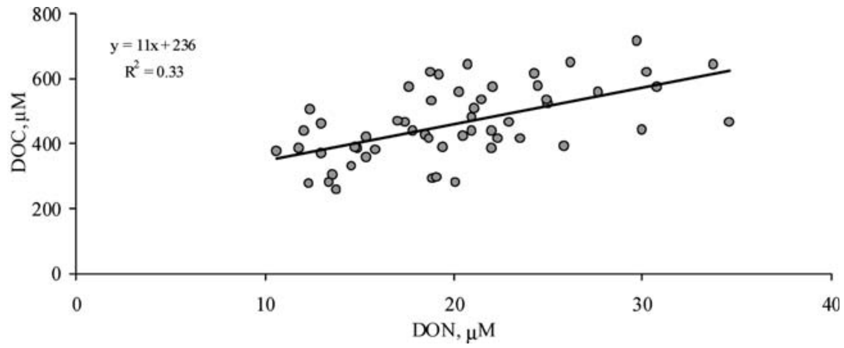

Figure 5. Dissolved organic nitrogen (DON) concentration (μM) as a function of dissolved organic carbon (DOC) concentration (μM). DOC data is from Fulweiler et al. 2003.

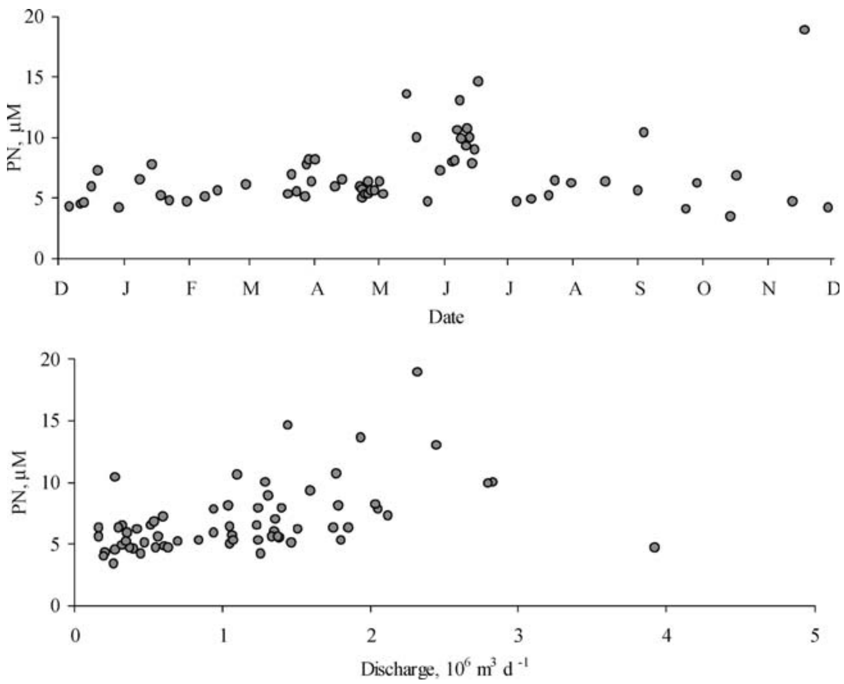

Figure 6. Particulate nitrogen (PN) concentration (μM) as a function of time and river discharge over the study period (12/06/01-11/29/02).

Phosphorus
There was no clear seasonal cycle in any of the phosphorus forms measured during this study (Figure 7a–c). DIP concentrations ranged from 0.29 to 3.2 μM, considerably higher than those summarized by Meybeck (1982) for unpolluted waters (0.03–0.77 μM). Burkholder and Sheath (1985) examined five Rhode Island rivers, including two streams above our sampling site, but within the Pawcatuck watershed (Chipuxet River and Moscow Brook), and found inorganic phosphorus to range between 0.04 and 0.11 μM. The University of Rhode Island's Watershed Watch Program has also monitored rivers within the Pawcatuck watershed north of our sampling site and the two point sources mentioned previously, and found low concentrations of dissolved inorganic phosphorus (0.10–0.13 μM). In an attempt to determine why the phosphate concentrations were so much higher at our sampling site, we used the NPDES data available for a 6 month period (April–September), to examine the phosphate flux to the river from the two point sources. We calculated a mean 6 month phosphate flux by multiplying the mean reported DIP concentration (39 μM $\pm$ 30 for Bradford and 5.5 mM $\pm$ 13.4 for Kenyon; mean $\pm$ SD) by the mean reported effluent discharge from each plant. During this period, Kenyon Piece Dye Works alone could potentially have increased

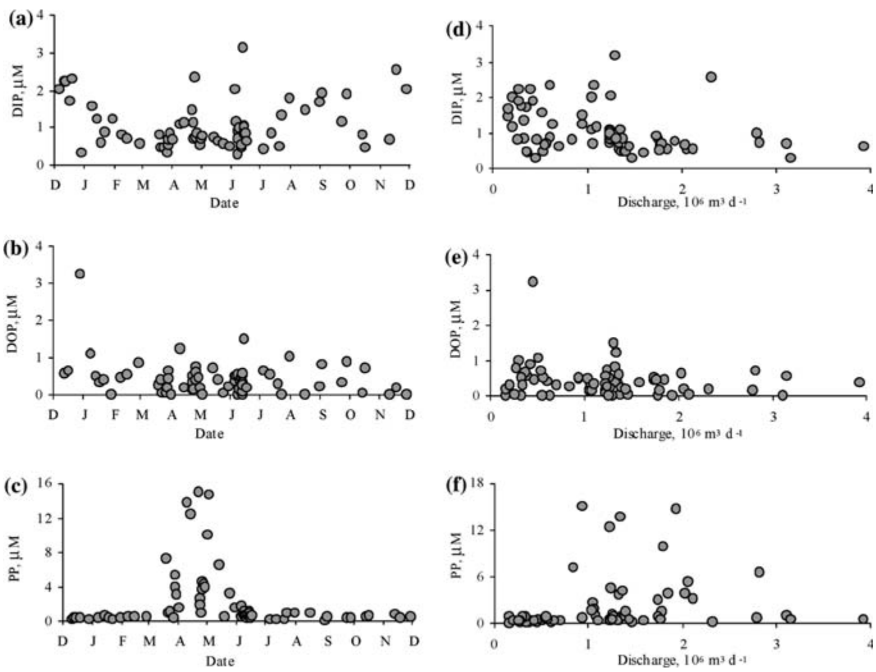

Figure 7. Dissolved inorganic phosphorus (DIP), dissolved organic phosphorus (DOP), and particulate phosphorus concentration (PP) (μM) as a function of time and river discharge over the study period (12/6/01–11/29/02).

DIP concentrations by 9.0 μM. Because phosphorus is easily adsorbed to sediment particles and may be rapidly sequestered by in-stream vegetation, we would not expect all of the phosphorus from these waste waters to reach our sampling site which is 29 km downstream from Kenyon and 13 km downstream of Bradford (Figure 1). DIP concentrations we measured at the mouth of the Pawcatuck did not exceed 3.15 μM, suggesting that there must be a strong sink for phosphorus within the river.

Concentrations of dissolved inorganic and organic phosphorus, as well as particulate phosphorus (PP), did not vary systematically with water discharge (Figure 7d–f). The high particulate phosphorus concentrations found during April and May did not correspond with elevated particulate carbon or particulate nitrogen concentrations (Fulweiler et al. 2003), nor were they always associated with increased river discharge.

TSS

The concentration of particulate matter ($>0.70\ \mu$m) in the Pawcatuck River did not vary in a regular way with season and generally increased with river discharge (Figure 8a–b). During the 7 months from May through November, when we also measured the approximate organic content of the suspended matter, the organic fraction varied from 40 to 100% of the total. Organic content decreased as a fraction of TSS as TSS concentrations increased (Figure 8c). There was a weak correlation between TSS and particulate nitrogen, but not with particulate phosphorus. At low concentrations of TSS, particulate nitrogen comprised between 5% and 10% of the total. This decreased at higher TSS concentrations (Figure 8d). Since TSS concentrations increase with discharge, fresh particulate matter may be re-suspended first from the streambed or carried to the river through overland flow. At higher water discharge, eroded sediments low in nutrients may comprise more of the total suspended matter.

Seasonal and annual fluxes

The annual export of total nitrogen, total phosphorus, and total suspended solids from the Pawcatuck watershed amounted to 16.0×10^6 mol y^{-1}, 0.97×10^6 mol y^{-1}, and 1.4×10^6 kg y^{-1}, respectively (Table 2). On an annual basis, DIN export was primarily comprised of nitrate (83%), with ammonium accounting for almost 13% (Table 2). The molar flux ratio of TN:TP was 16.5. About 55% of the suspended particulate solids were organic matter consisting of 3.2% N, on average.

The flux of all forms of nitrogen and TSS increased with increasing water discharge, while total phosphorus did not (Figure 9). The processes governing the behavior of N and P in the watershed are clearly different and result in export behavior that is more reliably estimated from discharge for nitrogen.

Seasonal fluxes of the various constituents showed that the majority of the annual fluxes of all forms of the nutrients measured were exported during April through June, during the period of peak water discharge (Figure 10). Elevated

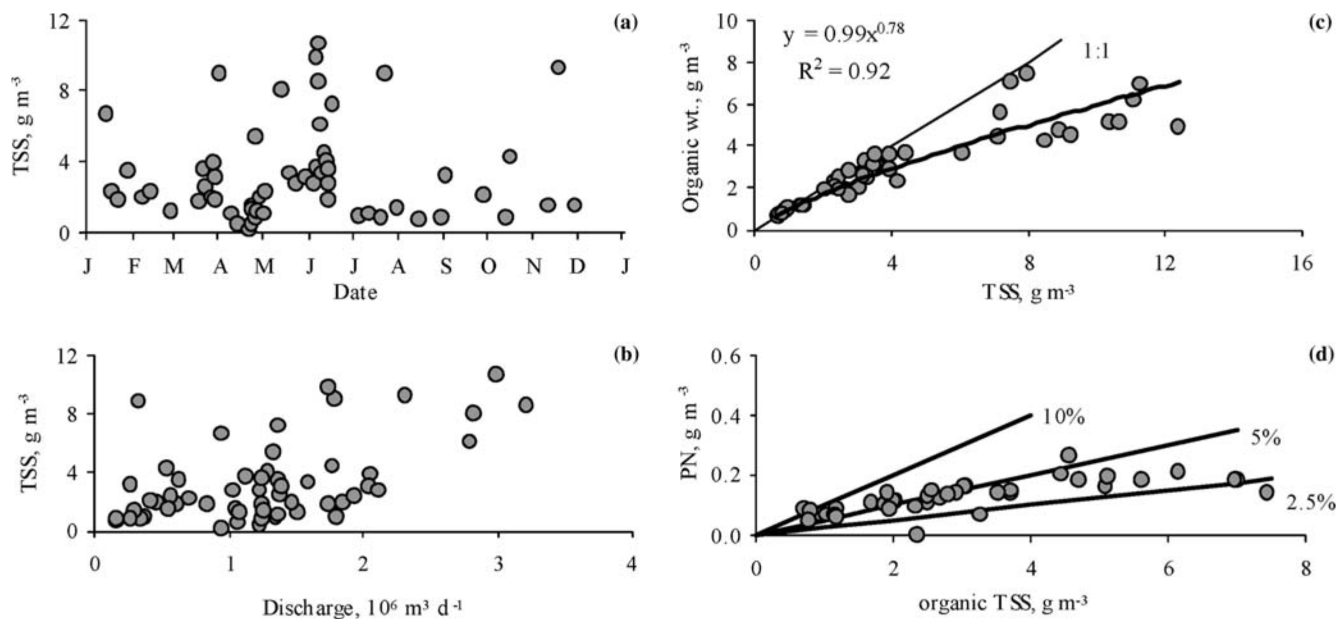

Figure 8. (a–b) Total suspended solid (TSS) concentration (gm^{-3}) as a function of time and river discharge over the study period (12/6/01–11/29/02); (c) Concentration of organic matter (gm^{-3}) in TSS (gm^{-3}) from May 2002 to November 2002; (d) Particulate nitrogen (PN) concentration (μM) as a function of organic component of the TSS.

Table 2. Estimates of the annual fluxes of nutrients and suspended solids from the Pawcatuck watershed to Little Narragansett Bay. Values were calculated using Beale's (1962) unbiased ratio estimator. Annual nutrient (10^6 mol y^{-1}) and suspended solids (10^6 kg y^{-1}) fluxes are for the period during December 1, 2001 and November 30, 2002.

$NH_4{}^+$	0.97	DIP	0.29
$NO_2{}^-$	0.13	DOP	0.08
$NO_3{}^-$	6.0	PP	0.65
DIN	7.2	TDP	0.30
DON	6.2	TP	0.97
TDN	13.3		
PN	2.8	TSS	1.4
TN	16.0	Organic solids	1.2

spring phosphorus fluxes were driven by the high flux of particulate phosphorus during this season, while elevated nitrogen fluxes were driven by an overall increase in each constituent. DIP flux was also elevated in autumn along with DON and PP. Conversely, dissolved inorganic nitrogen flux was high in winter along with DOP and PP.

North of the Pawcatuck watershed, much of the Rhode Island landscape is dedicated to residential, commercial, and industrial uses. For comparison, we examined the nutrient yields from five of these more densely populated watersheds as reported in Nixon et al. (1995). Anthropogenic sources are known to have a stronger effect on in-stream concentrations of DIN than DON (Campbell et al. 2000). In the northern Rhode Island Rivers, DIN comprises about 70% of the TN; in the Pawcatuck, DIN only accounted for 45% of the TN (Table 3). Recent studies have shown that more anthropogenically impacted temperate North American watersheds export more inorganic nitrogen, while less anthropogenically impacted temperate South American watersheds export mainly organic nitrogen (Hedin et al. 1995; van Breemen 2002; Perakis and Hedin 2002). The Pawcatuck River has a NO_3:DON ratio of 1 while in the urban Rhode Island rivers it is twice this. The ratio of NO_3:DON in pristine streams is close to 0.1, while it may reach 3 in some of the more degraded rivers of Asia, North America, and Europe (Caraco and Cole 1999b).

On average, total phosphorus in the Pawcatuck was composed of 30% DIP, 11% DOP, and 59% PP, compared to 62% DIP, 15% DOP, and 22% PP in the urban rivers. Over the annual cycle, the ratio of DIN to DIP export in the Pawcatuck was approximately 30, despite the strong phosphorus point source discharge to the river. This suggests that phosphorus might have been limiting to plant growth in the river. DIN:DIP fluxes for the more urban rivers studied by Nixon et al. (1995) ranged from 10 to 57, with a mean of 34. Not surprisingly, nutrient export per unit area is much lower in the Pawcatuck than it is from the other urban watersheds (Table 3). Overall, the urban rivers are approximately five times higher in total nitrogen and approximately three times higher in total phosphorus.

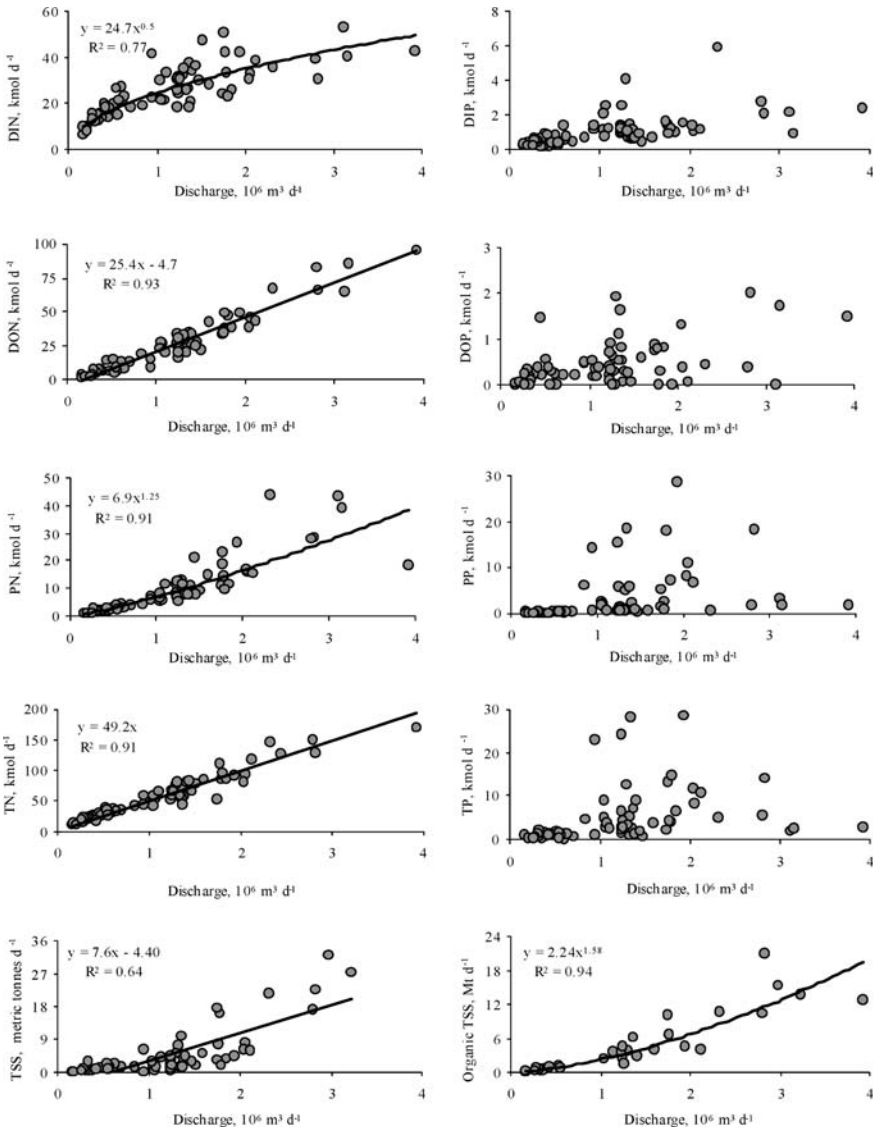

Figure 9. Fluxes (kmol d^{-1}) of nitrogen and phosphorus as a function of river discharge at the mouth of the Pawcatuck River over the study period (12/6/01–11/29/02). Total suspended solid (TSS) flux (metric tonnes d^{-1}) and the organic components of TSS flux (metric tonnes d^{-1}) as a function of river discharge as measured at the mouth of the Pawcatuck River. TSS and the organic component of TSS flux showed positive, non-linear correlations with water discharge that were highly significant ($p > 0.0001$).

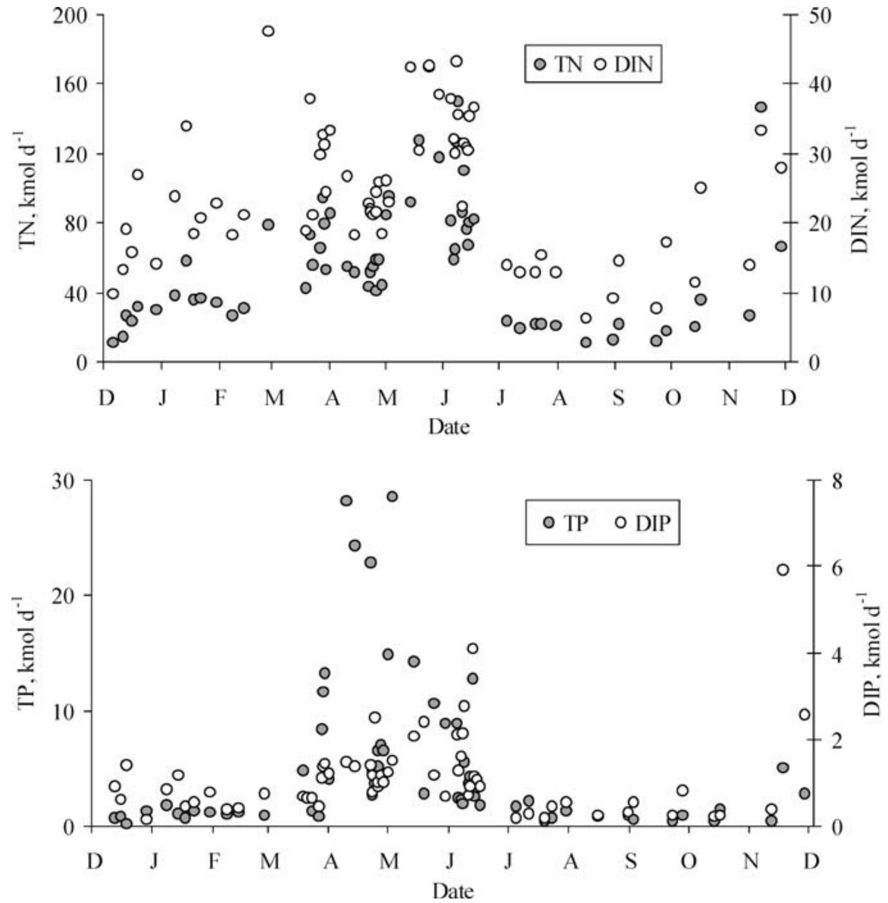

Figure 10. Total nitrogen (TN), dissolved inorganic nitrogen (DIN), total phosphorus (TP), and dissolved inorganic phosphorus (DIP) flux (kmol d^{-1}) over the study period from December 6, 2001–November 29, 2002.

Comparison of nutrient exports with a preliminary inventory of nutrient inputs to the watershed:

According to our very preliminary assessment, the Pawcatuck watershed exported about 12% of its total nitrogen and approximately 10% of its total phosphorus inputs during the study year (Table 4). This nitrogen value falls at the lower end of the export range of 11–40% reported for watersheds along the Atlantic Coast of the United States by Boyer et al. (2002). To understand how the decreased annual river discharge affected the nitrogen export from the Pawcatuck during this study, we used the robust relationship between total N flux and water discharge to estimate TN export using the 60 year mean daily discharge (1.46×10^6 m^3 d^{-1}). The result suggests that a more typical N loss would be about 34 kmol N km^{-2} y^{-1} or 20% of our estimated input to the watershed. Because TP and river discharge are not strongly related, we attempted to estimate a more typical TP flux using a simple average and TP concentration and the 60 year mean daily discharge. The result is not significantly different from the Beale's estimate for the study period. The nitrogen unaccounted for by river export could be sequestered in forest biomass (Bormann and Likens 1979; Howarth et al. 1996; Hooker and Compton 2003)

Table 3. Nitrogen and phosphorus export (kmol km^{-2} y^{-1}) from the Pawcatuck watershed and from five urban watersheds in Rhode Island and southeastern Massachusetts.

	Pawcatuck[a]	Blackstone[b]	Pawtuxet[b]	Woonasuatucket[b]	Moshassuck[b]	Taunton[c]
NH_4^+	1.3	28.6	41.6	12.7	13.1	20.6
NO_2^-	0.2	1.1	1.7	0.4	1.6	0.8
NO_3^-	7.9	49.1	33.3	36.6	41.0	37.8
DIN	9.4	78.9	76.5	49.6	55.7	59.2
DON	8.1	24.5	25.0	22.4	21.3	20.6
PN	3.7	4.1	5.0	4.5	4.9	0.7
TN	21	107	106	75	82	80
DIP	0.4	2.2	7.5	1.2	1.0	2.3
DOP	0.1	0.8	1.5	0.6	0.7	0.4
PP	0.9	1.3	1.2	0.9	0.8	1.0
TP	1.3	4.3	10	3.0	3.3	3.6

[a]Pawcatuck data from this study as predicted by Beale's unbiased estimate.
[b]Nixon et al. (1995).
[c]Annual fluxes reported in Nixon et al. (1995) are from Boucher (1991).

Table 4. Preliminary nitrogen and phosphorus budget for the Pawcatuck watershed.

	kmol N km^{-2} y^{-1}	kmol P km^{-2} y^{-1}
Input		
Human waste, septic[a]	17	0.96
Livestock waste[b]	50	4.1
Fertilizer[c]	14	3.4
Atmospheric deposition[d]	82	4.7
Industrial point source[e]	–	3.6
Total	163	12
Export		
River*	21	1.3
Percent exported in river	~12%	~10%

[a]Nixon et al. 2005. Mean N and P concentrations of raw sewage measured at Fields Pt. and Bucklin Pt. treatment facilities divided by population served.
[b]Nitrogen and phosphorus loads for cattle (dairy and beef), horses, sheep, and poultry (Stanley 1992). Country level livestock data from census of agriculture for 1997, http://www.govinfo/kerr.orst.edu/php/agri/area.php
[c]Rhode Island Department OF Environmental Management, Division of Agriculture: Fertilizer Use Summary (2001–2002) prorated from state level data.
[d]Nitrogen deposition: Luo et al. (Phosphorus) deposition: Yang et al. (1996).
[e]Environmental Protection Agency (2003), http://www.epa.gov/enviro/index_java.html
*River export from Table 3.

or soils (Nadelhoffer et al. 1999), denitrified within the watershed, especially in the many wetlands and marshes (Howarth et al. 1996; Schnabel et al. 1997; Gold et al. 2001), or removed through in-stream processes (Seitzinger et al. 2002b). The fate of P entering the watershed and not exported in the river is not known. Sequestration in forest and agricultural soils must be a major P sink (Hillbricht-Ilkowska et al. 1995).

Inputs to Little Narragansett Bay

Freshwater

The Pawcatuck River is the primary source of freshwater to Little Narragansett Bay, supplemented by two other small streams, unquantified groundwater flows, and direct deposition. Mastuxet brook is an ephemeral stream located in Rhode Island and Anguilla Brook drains a 31 km^2 wetland in Stonington, Connecticut. With a 90 year mean annual rainfall at Westerly, Rhode Island of 1.2 m, the small watershed of Anguilla Brook only receives about 36×10^6 m^3 y^{-1} of precipitation. Assuming a 40% loss in evapotranspiration (Hanson 1991), Anguilla Brook may add less than 22×10^6 m^3 y^{-1} of freshwater to Little Narragansett Bay, or less than 5% of the total annual Pawcatuck River discharge (530×10^6 m^3 long-term mean, Table 5). During this study, the two treatment plants which discharge directly into Little Narragansett Bay contributed a total of 4.6×10^6 m^3 of freshwater or 1.5% of the Pawcatuck River total discharge.

Nutrients

Based on an intensive 2 year evaluation of N and P discharge from the main sewage treatment plants in Rhode Island, we found the average nitrogen and phosphorus concentration in raw effluent to be 0.9 mol N and 3.2 mmol P per person per day (Nixon et al. 2005). Using these mean values and the number of people served by the two wastewater treatment plants, we estimate that these facilities add approximately 6.0×10^6 mol N y^{-1} and 0.21×10^6 mol P y^{-1}.

Table 5. Freshwater, total nitrogen, and total phosphorus inputs to Little Narragansett Bay from the Pawcatuck River, Anguila brook, wastewater treatment facilities, and direct deposition. Freshwater units are 10^6 m^3 y^{-1}. N and P units are 10^6 mol y^{-1}.

	Freshwater	N*	P
Pawcatuk River	530	26	0.97
Anguila Brook	22	–	–
Waste water treatment facilities	4.6	6.0	0.21
Direct deposition	11	0.1	0.2
Total	567.6	32	1.4

*The nitrogen value used in that calculated from the regression found from this study (Figure 9) and the 60 year mean discharge (1.46×10^6 m^3 day^{-1}).

Dry atmospheric N deposition is 15–40% less on surface water bodies than on the corresponding watersheds, because water bodies are much smoother with low drag coefficients (Meyers et al. 2001). Using the average reduction rate (27.5%) of atmospheric deposition on surface waters, we calculated atmospheric direct deposition to Little Narragansett Bay to be approximately 59 kmol N km^{-2} y^{-1}. P deposition remained as it was in the watershed at 150 mol P km^{-2} y^{-1} (Yang et al. 1996).

The low population density and high percentage of forest in the Pawcatuck watershed combined with the high watershed nitrogen retention (~88%) might lead one to assume that Little Narragansett Bay is not intensively enriched with nitrogen. However, compared to other estuaries along the North Atlantic coast, Little Narragansett Bay receives a large amount of both nitrogen and phosphorus per unit area of estuary (Table 6). The watershed of Narragansett Bay proper is 44% forest, 7% agriculture, and 30% developed (Crawley et al. 2000) with an overall population density of 426 people per km^{-2}. Area-specific nitrogen and phosphorus input to Little Narragansett Bay is 14% and 8% higher, respectively, than it is to Narragansett Bay, despite the high population density and intensive development of the Narragansett Bay proper watershed. The shallower depth of Little Narragansett Bay (2 m compared with 8.6 m in Narragansett Bay) also leads to a volume specific nutrient loading that is four times greater in Little Narragansett Bay than in Narragansett Bay. This apparent discrepancy can be explained by the difference in the land area to water area ratio of these two systems. Little Narragansett Bay has a land area to water area ratio of 80 compared to that of 14 for Narragansett Bay proper. Therefore, despite the high percentage of forest and the low population density found in the Pawcatuck watershed, Little Narragansett Bay still receives a high amount of N per unit area. The impact of these nutrient loadings may be mitigated, at least to some extent, by the relatively short residence time of the water in the bay. Using surface and bottom salinity data collected at seven stations in Little Narragansett Bay during the summer of 2002,

Table 6. Total nitrogen and total phosphorus loading to various estuaries along the east cost of the United States. Units are kmol km^{-2} of water surface y^{-1}.

	N	P
Chincoteague Bay[a]	218	7
Greenwich Bay, RI[c]	631	67
Chesapeake Bay[b]	938	41
Delaware Bay[b]	1900	115
Narragansett Bay[b]	1960	115
Potomac Estuary[b]	2095	44
Little Naragansett Bay[d]	3326	146

[a]Boynton et al. (1993).
[b]Nixon et al. (1996).
[c]Granger et al. (2000).
[d]From Table 5.

freshwater inflow, and the freshwater fraction method outline in Ketchum (1969), we estimated a residence time of only 3 days. This contrasts with the mean summer residence time in Narragansett Bay of about 34 days (Pilson 1985).

TSS

TSS discharged to Little Narragansett Bay amounted to approximately 3.8 t day^{-1} or almost 1400 t y^{-1}. This represents an export of 1.8 t of solids km^{-2} of watershed per year. Only about 15% of this is inorganic sediment. If the inorganic material were evenly distributed over Little Narragansett Bay, approximately 22 g m^{-2} y^{-1} would be deposited. However, it is more likely that much of the sediment would be deposited directly below the Pawcatuck River, in a 1.9 km^2 area known locally as the Pawcatuck estuary, where it would provide a deposition of 110 g m^{-2} y^{-1}. Assuming a sediment bulk dry density of 2.56 g cm^{-3} and sediment water content of 50% (Beach 1981) this would result in a shoaling of the Pawcatuck estuary of about 0.8 mm y^{-1}. Using our TSS flux verse discharge regression and long-term USGS water discharge, we calculate a 23 year mean watershed TSS yield of 6.0 t km^{-2} y^{-1}. Long-term sediment input may therefore shoal the Pawcatuck estuary by about 2.8 mm y^{-1}.

Comparison of measured and modeled N and P Export

Predictive empirical regression models of nitrogen and phosphorus export from watersheds rely on a variety of drainage basin characteristics, including population density, fertilizer application, atmospheric deposition, runoff, total nitrogen inputs, etc. (Peierls et al. 1991; Caraco 1995; Howarth et al. 1996; Caraco and Cole 1999b; Boyer et al. 2002). Because this study took place, at least in part, during a relatively dry period, we used the nitrogen flux values calculated from the strong relationship between N flux and discharge to compute a more typical N flux to compare with N export predicted by various regression models. A simple regression model based on human population density (Peierls et al. 1991) predicts a nitrate export which is only 40% of our value for long term nitrate flux. However, the Caraco and Cole (1999b) nitrate export model, which estimates nitrate export from population density, runoff, and N export coefficients, only underestimates our calculated flux by 15%. Boyer et al. (2002) used total watershed nitrogen inputs to predict riverine total nitrogen export. Their regression only overestimates the long term N export from the Pawcatuck by 17%. The agreement of the Caraco and Cole (1999b) and the Boyer et al. (2002) regressions with our measured nitrate and TN fluxes is impressive and particularly so because, the Pawcatuck watershed is much smaller than most (98%) of the watersheds used to develop the regressions. Caraco (1995) reports that watershed population accounts for 47% of the variation in soluble reactive phosphate export in the 32 rivers she summarized.

However, the empirical regression she developed predicts only 25% of the measured phosphate export from the Pawcatuck watershed. This is most likely because of the strong industrial point source addition of phosphate to the Pawcatuck River.

Conclusions

A highly resolved annual cycle for all forms of nitrogen and phosphorus, as well as TSS, allowed us to evaluate the importance of seasonality and river discharge on the concentrations and annual fluxes of each of these constituents. Our data indicate that nitrogen concentrations and annual fluxes can be reliably predicted by river discharge alone. Phosphorus did not exhibit this behavior, and measurements are required to evaluate its flux from the watershed.

As in many areas in the northeast, the largest N input to the Pawcatuck watershed is atmospheric deposition. The Pawcatuck watershed sequestered or returned to the atmosphere approximately 88% of the nitrogen and 90% of the phosphorus it received during the study period. With more normal hydrology, the nitrogen value might be closer to 80%. These values are at the lower end of the spectrum reported by Boyer et al. (2002) in a study of 16 northeastern watersheds. While the nitrogen retention/removal rate is impressive, Little Narragansett Bay is still a heavily nitrogen enriched system. In fact, in comparison to six other estuaries along the east coast of the United States, it receives the most nitrogen and the second most phosphorus on an area basis. On a specific volume basis, it is four times more intensively enriched with N than Narragansett Bay.

Empirical models based on overall watershed characteristics (i.e. nitrogen loading rate, population density, etc.) were used to examine annual fluxes from the watershed. The Boyer et al. (2002) model, which uses nitrogen load per area to the watershed, overestimated by 50% the amount of nitrogen exported over the period of this study. However, when compared to N export for a year with more average river discharge, their method overestimated N export by less than 20%. The model of Caraco and Cole (1999b) was also consistent with our measurements, but underestimated long-term N discharge by about 15%. Site specific concentration measurements provide a powerful tool to observe processes occurring within watersheds, while the general models appear to provide valuable assessments of nitrogen export across a wide range of watersheds.

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