

## **An assessment of the annual mass balance of carbon, nitrogen, and phosphorus in Narragansett Bay\***

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**Abstract.** Narragansett Bay is a relatively well-mixed, high salinity coastal embayment and estuary complex in southern New England (USA). Much of the shoreline is urban and the watershed is densely developed. We have combined our data on C, N, and P inputs to this system, on C, N, and P accumulation in the sediments, and on denitrification with extensive work by others to develop approximate annual mass balances for these elements. The results show that primary production within the bay is the major source of organic carbon (4 times greater than other sources), that land drainage and upstream sewage and fertilizer are the major sources of N, and that landward flowing bottom water from offshore may be a major source of dissolved inorganic phosphorus. Most of the nutrients entering the bay arrive in dissolved inorganic form, though DON is a significant component of the N carried by the rivers. About 40% of the DIN in the rivers is in the form of ammonia. Sedimentation rates are low in most of Narragansett Bay, and it appears that less than 20% of the total annual input of each of these elements is retained within the system. A very small amount of C, N, and P is removed in fisheries landings, denitrification in the sediments removes perhaps 10–25% of the N input, and most of the carbon fixed in the system is respired within it. Stoichiometric calculations suggest that some 10–20% of the organic matter formed in the bay is exported to offshore and that Narragansett Bay is an autotrophic system. Most of the N and P that enters the bay is, however, exported to offshore waters in dissolved inorganic form. This assessment of the overall biogeochemical behavior of C, N, and P in the bay is consistent with more rigorously constrained mass balances obtained using large living models or mesocosms of the bay at the Marine Ecosystem Research Laboratory (MERL).

### **Introduction**

A fundamental problem in any natural science is the establishment of the relevant conservation equations. In marine geochemistry these take the form of mass, or better, flux balances. Significant effort has gone into establishing the river input in these balances, however, only recently has the importance of estuarine processes to the net value of the fluvial flux been recognized. (Edmond et al. 1981)

In what may have been the first attempt to develop the framework for an elemental mass balance in a marine ecosystem, James Johnstone (1908) considered the nitrogen budget for the North Sea as it was at the turn of the

century. While he could not quantify some of the important processes, he included all of the terms we recognize today. Despite that promising beginning, however, and the benefit of 90 years of progress in obtaining physical and biological rate measurements in the sea, no fully closed annual mass balance for the major biologically important elements has yet been achieved for a marine system of any size and complexity.

We define a closed budget as one in which all of the inputs to, and all of the outputs from, a system are measured independently over the same period of time and found to balance. If the inputs and outputs do not agree, the budget can only be closed by independent measurements of net changes in the amount of the material of interest within the system. The great and simple power of such a budget is that the conservation of mass provides a final unequivocal constraint against which the combined forces of ignorance, error, and omission must come to rest and be reconciled or, at the very least, recognized.

In the few marine and estuarine systems where comprehensive inventories of elemental fluxes have been assembled, the practice has been to assume a closed budget and to calculate at least one major term of the balance by difference. While this provides an economical and practical alternative to the measurement of fluxes that may be tedious or virtually impossible to quantify, it also sacrifices much of the rigor of the mass balance approach. Even in less than ideal form, however, the framework of an annual elemental budget is a powerful tool for understanding biogeochemical processes at the land-sea interface.

In this paper we describe the present state of knowledge regarding the annual mass balance of organic carbon, nitrogen, and phosphorus in Narragansett Bay, an urban estuary and coastal embayment complex in Rhode Island and Massachusetts (USA). In spite of the fact that we can not claim to have closed the budget for any of these elements, it is possible and useful to assess the relative importance of various sources and sinks, to gain some perspective on the way in which anthropogenic fluxes from land may be modified before reaching the coastal ocean, and to compare the behavior of this system with others that have been evaluated in a similar way.

### *Narragansett Bay*

Various authors have defined the boundaries of Narragansett Bay in different ways (Pilson 1985a). For this exercise we include Narragansett Bay proper (the East and West Passages from the mouth to Conanicut Point, including side bays and harbors), the Providence and Seekonk River estuary, and Mt. Hope Bay and the Taunton River estuary (Fig. 1). We exclude the Sakonnet River, which has only a restricted hydraulic connection with the rest of the

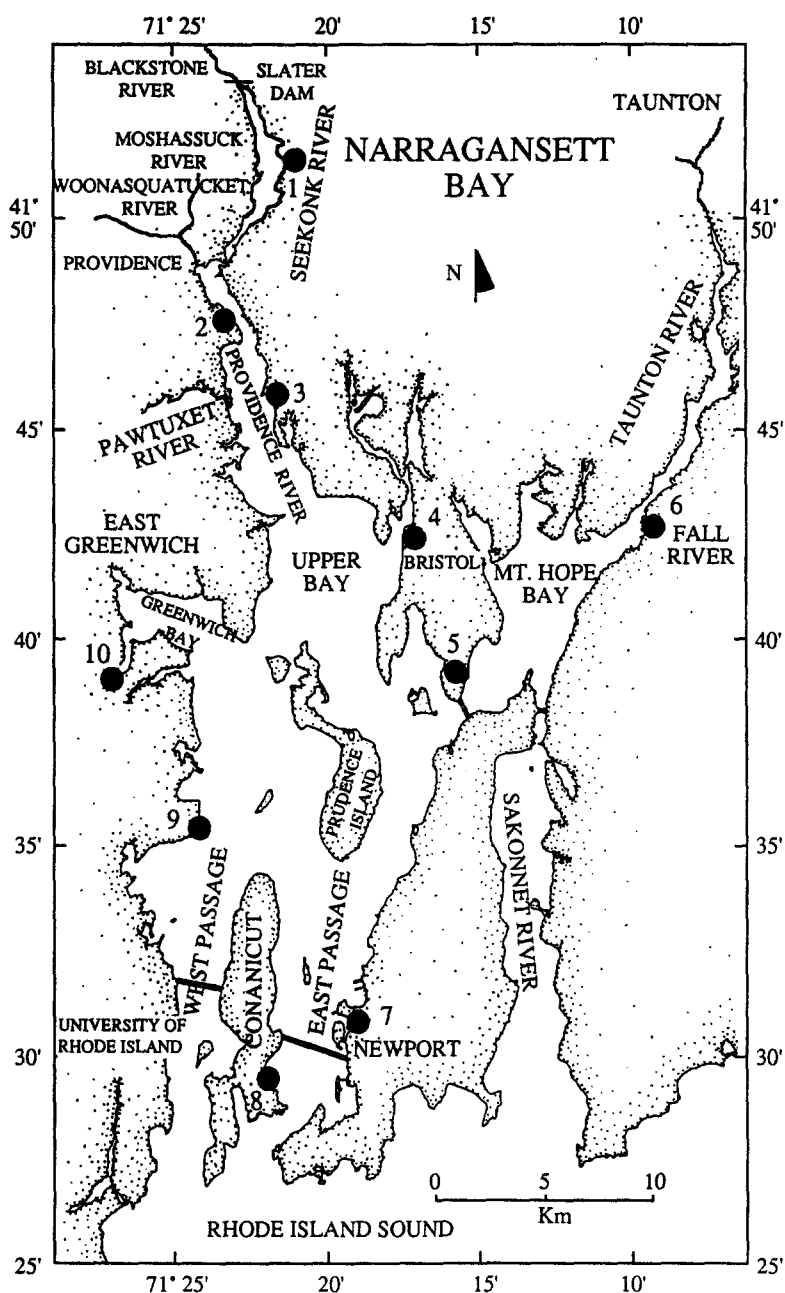


Fig. 1. Narragansett Bay and its major tributaries. The Seekonk and Providence Rivers are actually estuaries and the Sakonnet River is a well-mixed marine embayment. Numbered locations are sewage treatment plants that discharge directly to the bay: (1) Bucklin Point, (2) Fields Point, (3) East Providence, (4) Bristol, (5) Warren, (6) Fall River, (7) Newport, (8) Jamestown, (9) Quonset Point, (10) East Greenwich.

bay and receives very little fresh water inflow or sewage effluent. Defined in this way, the water area of the bay is 328 km<sup>2</sup>, with a mean depth of 8.6 m (Pilson 1985a; Chinman & Nixon 1985).

The average total fresh water input to the bay is only about 105 m<sup>3</sup> s<sup>-1</sup> (Pilson 1985a; Ries 1990) and, with the exception of the Taunton River, the great majority of that enters the bay over dams. As a result, the Taunton River estuary is the only area with a significant low salinity estuarine mixing zone. Most of the bay is well-mixed or only weakly stratified, with salinities in the bay proper usually ranging between 27–31 p.s.u. Turbidity is low and suspended sediments are usually less than 5 g m<sup>-3</sup> in waters below Conimicut Point. Narragansett Bay contains a phytoplankton based ecosystem with little salt marsh or macroalgae. The flushing rate of the system averages 26 days (Pilson 1985a). A more detailed description of the bay and its ecology is given in Kremer & Nixon (1978).

## **The data base**

The bay budgets can not be closed in a formal sense because there have been no measurements of the net fluxes of materials at the mouth of the system and because the measurements of other inputs, outputs, and changes in storage are not contemporaneous. Aside from these significant, but common, limitations, data are available to address all of the other major terms of the budgets, though with different levels of confidence.

### *Inputs*

#### *Atmospheric deposition*

The deposition of phosphorus from the atmosphere was measured at the Graduate School of Oceanography on the lower West Passage of the bay during 1975 (Graham 1977).

The wet deposition of nitrate and ammonium from the atmosphere was measured at a station on Prudence Island (Fig. 1) during 1989 and part of 1990, and dry deposition was calculated from contemporaneous measurements of nitric acid vapor and nitrate aerosol (Fraher 1991). We estimated the deposition of dissolved organic nitrogen from nitrate deposition using data obtained during 1985 and 1986 at the Graduate School of Oceanography by Nowicki & Oviatt (1990).

#### *Rivers*

We measured the concentrations of dissolved and particulate organic carbon (DOC and POC), reactive phosphate (DIP), dissolved organic phosphorus

*Table 1.* Analytical methods used to measure C, N, and P in rivers and sewage treatment plant effluents entering Narragansett Bay.

|  |   |
|--|---|
| Dissolved* inorganic phosphorus (DIP)                  | Murphy & Riley (1962)                       |
| Dissolved* organic phosphorus (DOP)                    | Valderrama (1981)                           |
| Particulate phosphorus (PP)                            | Solorazano & Sharp (1980)                   |
| Ammonia* (NH <sub>4</sub> )                            | Solorazano (1969)                           |
| Nitrite (NO <sub>2</sub> ) Nitrate* (NO <sub>3</sub> ) | Morris & Riley (1963)                       |
|  | Wood et al. (1967)                          |
| Dissolved* organic nitrogen (DON)                      | Valderrama (1981)                           |
| Particulate nitrogen (PN)                              | Carlo Erba Model<br>1106 Elemental analyzer |
| Dissolved* organic carbon (DOC)                        | Salonen (1979)                              |
|  | Horiba PIR 2000                             |
|  | Infrared gas analyzer                       |
| Particulate organic carbon (POC)                       | Carlo Erba Model<br>1106 Elemental analyzer |

\* Passing through Gelman AE filters.

(DOP), particulate phosphorus (PP), ammonium (NH<sub>4</sub>), nitrite (NO<sub>2</sub>), nitrate (NO<sub>3</sub>), dissolved organic nitrogen (DON), and particulate organic nitrogen (PN) in four of the larger rivers approximately every two weeks during 1982 and 1983. The analytical methods used are summarized in Table 1. With the exception of DOC, the same constituents were measured monthly in the Taunton River during 1988 and 1989 by Boucher (1991).

Taken together, the five rivers in which measurements were made account for about 75% of the total surface fresh water input to the bay (Table 2, Ries 1990). The average discharge during each day in which water samples were collected for analysis was reported by the U.S. Geological Survey from gauging stations set various distances upstream of our sampling stations, which were located just above the last dam before tidal water (Blackstone and Pawtuxet Rivers) or in fresh water above salt intrusion (Woonasquatucket and Moshassuck Rivers). Boucher (1991) sampled the Taunton River in free flowing fresh water between Taunton and North Dighton, Massachusetts. We increased the measured water discharges to account for the area of watershed below each gauge using ratios calculated by Pilson (1985a) and Boucher (1991). Direct groundwater discharge is not thought to be significant in Narragansett Bay.

There are a variety of ways to combine a relatively small set of concentration measurements with a large set of daily flow data to estimate an annual constituent flux (for example, see Dolan et al. 1981; Bierman et al. 1988).

Table 2. Long-term<sup>1</sup> mean annual freshwater input to Narragansett Bay from land drainage (Ries 1990).

|  | Drainage area km <sup>2</sup> | Discharge m <sup>3</sup> s <sup>-1</sup> |
|--|-------------------------------|--|
| <i>Rivers where C, N, and P were measured over an annual cycle</i> |                               |  |
| Taunton River  | 1455                          | 29.7                                     |
| Blackstone River   | 1222                          | 24.4                                     |
| Pawtuxet River   | 601                           | 11.7                                     |
| Woonasquatucket River  | 134                           | 2.8                                      |
| Moshassuck River   | 61                            | 1.2                                      |
|  | 3473                          | 69.8                                     |
| <i>Rivers without C, N and P data</i>                              |                               |  |
| Ten Mile River   | 143                           | 3.1                                      |
| Palmer River   | 123                           | 2.7                                      |
| Smaller rivers and coastal drainage                                | 602                           | 16.6                                     |
| Diversions   | —                             | 2.3                                      |
|  | 868                           | 24.7                                     |
| Total  | 4341                          | 94.5*                                    |

<sup>1</sup> Calculated from records for 13 stations that had data records ranging from 21 to 62 years.

\* There are additional freshwater inputs amounting to about 12 m s<sup>-1</sup> from direct precipitation on the surface of the bay and 4 m<sup>3</sup> s<sup>-1</sup> from sewage treatment plant discharges.

By sampling the rivers at a fixed time interval we captured only some of the higher discharges associated with winter storms (Fig. 2), so it was not appropriate to simply extrapolate between flux measurements or to use average values. Within the range of discharge conditions measured there were excellent correlations between water flow and nutrient flux for some constituents in some rivers, (e.g., Fig. 3) but not for others (e.g., Fig. 7). As a result, it was not possible to use a rating curve approach. For these reasons we chose to use Beale's flow-weighted unbiased estimate (Beale 1962; Canadian Centre for Inland Waters 1979) to calculate annual fluxes from the biweekly concentration measurements and daily flow data collected during one calendar year of measurement. This technique has been adopted by the International Joint Commission for calculating tributary nutrient inputs to the Great Lakes.

#### *Urban storm water runoff*

The concentrations of dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorus (DIP) in urban storm water runoff from four land use

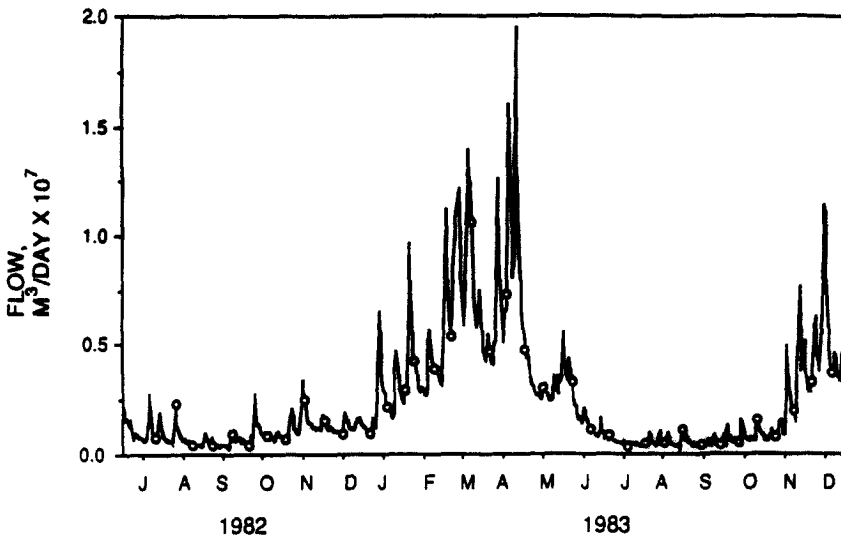


Fig. 2. Estimated mean daily discharge at the mouth of the Blackstone River during the time when we measured the concentrations of C, N, and P in the river. Days on which concentration measurements were made are shown with open circles.

categories in upper Narragansett Bay were measured through 12 storms during late 1979 and 1980 by Hanson (1982). She provided estimates of the annual flux of DIN and DIP per unit area of each land use type per unit of precipitation (Table 3). We multiplied these nutrient loss coefficients by the long-term mean precipitation around the bay ( $1.19 \text{ m y}^{-1}$ , Pilson 1989) and by the total area of each land use type in the cities and towns that discharge their storm water directly into the bay (Table 4) to estimate a total direct input of DIN and DIP from this source. Storm water from other urban areas in the watershed is included in the measured nutrient fluxes in the rivers draining to the bay. We calculated the total N and P lost from each land use type by applying the total N to DIN and total P to DIP ratios reported by the National Urban Runoff Program (Schueler 1987).

#### *Sewage treatment plants*

There are 32 sewage treatment facilities that discharge domestic and industrial waste water within the Narragansett Bay drainage basin. Twenty-two of these release their effluents into rivers and streams, and their contribution to the bay is included in the rivers where measurements of C, N, and P flux were obtained. Nine of the remaining plants discharge directly into the tidal waters of the Seekonk-Providence River estuary or into Narragansett Bay proper, and one discharges into Mt. Hope Bay (Fig. 1).

*Table 3.* The flux of DIN and DIP in urban storm water runoff from different land uses<sup>1</sup> in upper Narragansett Bay. Data are based on analyses of 12 storms during 1979–1980 (Hanson 1982). Units are  $10^3$  moles  $\text{km}^{-2} \text{y}^{-1}$  assuming precipitation of  $119 \text{ cm y}^{-1}$ , the long-term mean (Pilson 1989).

|             | DIN | DIP |
|-------------|-----|-----|
| Residential | 70  | 1.1 |
| Commercial  | 7.6 | 0.2 |
| Industrial  | 29  | 1.4 |
| Highway     | 120 | 44  |

<sup>1</sup> Descriptions of each classification are given by Hoffman et al. (1983).

*Table 4.* The extent of different types of developed land use in major urban/suburban areas adjacent to Narragansett Bay. The estimates are for different time periods between about 1975 and 1990 and should be considered only as rough approximations. Units are  $\text{km}^2$ .

|   | Residential | Commercial | Industrial | Highway |
|---|-------------|------------|------------|---------|
| Seekonk River, Providence River, Upper Bay <sup>1</sup> | 76          | 20         | 112        | 7.5     |
| Fall River <sup>2</sup>                                 | 15          | 3          | 3.7        | 3.6     |
| Newport <sup>2</sup>                                    | 7.2         | 1.1        | 0.02       | –       |
| East Greenwich <sup>2</sup>                             | 12          | 1.2        | 1.1        | 23.2    |
| North Kingstown <sup>2</sup>                            | 24          | 2.5        | 3.4        | –       |
| Total   | 134.2       | 27.8       | 120.22     | 34.3    |

<sup>1</sup> From Hoffman et al. (1983) who also describe the use categories. We have assumed that one-half of the area they describe discharging to the Blackstone River/Seekonk River actually goes to the Seekonk.

<sup>2</sup> From respective town or city planning offices.

During 1983, we collected biweekly grab samples of final effluent from each of the three largest treatment plants that discharge directly to the Seekonk-Providence River estuary and analyzed them for the same constituents measured in the rivers. The volume of effluent discharged each day was reported by the treatment plants and we calculated annual nutrient fluxes using Beale's unbiased estimation technique (Beale 1962).

The effluents we analyzed account for about 85% of the average daily direct discharge of sewage to the Narragansett Bay-Mt. Hope Bay system (Table 5). The remaining treatment plant effluents were analyzed for total



*Table 5.* Volume of effluent discharged directly into Narragansett Bay by publicly owned sewage treatment plants. Data for R. I. plants from R. I. Department of Environmental Management, RIPDES files.

|   | 1986 Average daily flows          |         |
|---|-----------------------------------|---------|
|   | $10^3 \text{ m}^3 \text{ d}^{-1}$ | Percent |
| Seekonk River <sup>1</sup>                            |                                   |         |
| Blackstone Valley District Commission (Bucklin Point) | 78                                | 22      |
| Providence River <sup>1</sup>                         |                                   |         |
| Narragansett Bay Commission (Fields Point)            | 195                               | 56      |
| East Providence                                       | 22                                | 6       |
| West Passage  |                                   |         |
| East Greenwich  | 3                                 | <1      |
| Quonset   | 3                                 | <1      |
| East Passage  |                                   |         |
| Warren  | 6                                 | 2       |
| Bristol   | 8                                 | 2       |
| Jamestown   | 2                                 | <1      |
| Newport   | 32                                | 9       |
| Mt. Hope Bay <sup>2</sup>                             |                                   |         |
| Fall River  | 73                                | 21      |
| Total   | 349                               |         |

<sup>1</sup> Concentrations of C, N, and P measured every two weeks as part of this study. Other plants measured 3–4 times (Pilson and Hunt 1989).

<sup>2</sup> Flow data from Hoffman (1987).

N and total P on three or four occasions during 1985–1986 (Pilson & Hunt 1989). We simply averaged the three or four daily fluxes for each of these plants and multiplied by 365. Since Pilson & Hunt (1989) also analyzed the same effluents we sampled much more intensively three years earlier, it is possible to compare the estimates based on 3–4 samples with those derived from 26 samples.

### *Primary production*

In spite of the large number of studies on various aspects of the phytoplankton of Narragansett Bay, there has been no comprehensive bay-wide survey of carbon fixation using modern  $^{14}\text{C}$  techniques (Hinga et al. 1989). The most common value cited is from water samples collected during 1974 from the mid West Passage (Furnas et al. 1976). More recent measurements were carried out in the lower West Passage over three annual cycles from 1978–1980 (Keller 1988).

### *Outputs*

Since no measurements of any constituent fluxes have been made at the mouth of the bay, we are left to account for fluxes from the bay to the atmosphere and from the bay to the land in fisheries harvest. There has been no significant dredging in which sediments and associated nutrients were removed from the bay since 1975.

### *Denitrification*

Denitrification rates in the sediments of Narragansett Bay were measured over an annual cycle in 1979 at three stations located near the mouth of the Providence River, near the middle of the bay, and just outside the mouth of the West Passage (Seitzinger et al. 1984). More recently, Nowicki (1994) employed a modification of the technique used earlier in the bay and measured the denitrification rate of mid bay sediments at 18 °C. She then combined empirical regressions relating sediment denitrification rates in large mesocosms to temperature with the annual cycle of water temperature observed in the bay to extrapolate from her summer data to an annual estimate of denitrification. No measurements of denitrification have been made in the East Passage, in Mount Hope Bay, or in the Seekonk-Providence River estuary (Fig. 1). Measurements in nutrient enriched Narragansett Bay mesocosms have shown much higher rates of denitrification (Seitzinger & Nixon 1985; Nowicki & Oviatt 1990), and Nowicki (1994) applied a temperature-denitrification regression from eutrophic mesocosm sediments to the area of sediment contained in the Seekonk-Providence River estuary when calculating her average bay-wide annual estimate.

Anoxic bottom water is found only intermittently in very restricted areas of the Providence-Seekonk River subsystem (Granger 1994), and it does not appear that denitrification in the water column is of any significance in Narragansett Bay.

### *Fisheries landings*

The only commercial fishery of importance in the bay is that for the hard clam, *Mercenaria mercenaria*. Since 1980 the landings of this species have averaged about  $1.75 \times 10^6$  kg y<sup>-1</sup> fresh weight of meat. Some menhaden are also taken in the bay during some years, and there are recreational fisheries for several finfish species. These landings have never been adequately quantified. Even if they were known, it is not clear how much of the biomass of each species is actually produced in Narragansett Bay and how much is a growth increment acquired offshore or in other embayments. As a practical matter, the finfish landings are a small term in the budgets, and we limited our calculations to the clam fishery.

## *Changes within the bay*

### *The water column*

Unlike the Baltic Sea, where significant amounts of nutrients have been accumulating in the water column (Larsson 1986), there do not appear to have been any secular trends in water column nutrient concentrations in Narragansett Bay, at least since about 1960 (Nixon & Lee 1979; Pilson 1985b). This is consistent with an historical reconstruction of nutrient inputs to the bay which suggests that the major increase in nutrient discharges to this urban estuary occurred around the turn of the century, as sewer systems were installed (Nixon 1989, 1995). An extensive review by Hinga et al. (1989) found "no discernable trends" in phytoplankton abundance in the bay during the past 35 years.

### *Sediments*

Since it is likely that most or all of the sediment that enters Narragansett Bay is trapped within the system (Meade 1982), the accumulation of sediment and associated nutrients is a potentially significant storage term in the annual C, N, and P budgets. It is important to distinguish here between the short-term deposition of organic matter on the bottom and the long-term accumulation or burial of sediments. Nutrients associated with the former are largely remineralized and returned to the overlying water within an annual cycle (Garber 1984; Kelly & Nixon 1984; Nowicki 1991). On the other hand, a small fraction of the C, N, and P contained in the organic matter and/or carbon and nutrients taken up from the water and/or present on the sediments when they entered the bay will be buried with the inorganic material as it accumulates over time. This latter flux is the term of interest for the budgets.

No direct measurements of sediment input to Narragansett Bay have been reported. Boucher (1991) obtained monthly measurements of the concentrations of total suspended matter and inorganic sediments over the 1989 annual cycle in the Taunton River, and her data can be used to estimate the sediment flux into the Taunton estuary and Mt. Hope Bay. For the rest of Narragansett Bay, we must rely on extrapolations from cores of sediment collected in various ways and "dated" using a variety of geochemical markers and modeling assumptions.

Santschi et al. (1984) reviewed the data from 14 cores collected between 1974 and 1980. At that time, no cores had been taken from the Seekonk-Providence River area, Greenwich Bay, Mt. Hope Bay, or the mid and lower reaches of the East Passage (Fig. 1). A more recent study by Corbin (1989) provided accretion rate estimates from eight sites including the Seekonk-Providence River and Greenwich Bay. Sedimentation rates for these sites were

based on the concentrations of  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  at various depths in sediment cores as determined by Dr. Peter Appleby at the University of Liverpool, UK. The radiometric dating was further constrained by measurements of the concentrations of eight specific organic pollutants and several metals at various depths in the sediment compared to the history of anthropogenic inputs of the pollutants (Corbin 1989).

The concentrations of C, N and P on sediments below the enriched zone of bioturbation ( $\sim 10\text{--}15$  cm, Nixon et al. 1986a) have been measured in upper Narragansett Bay proper, at mid bay, and in the lower West Passage (Beach 1981; Garber 1982; Nixon & Pilson 1984; Frithsen et al. 1985; Nixon et al. 1986a). Corbin (1989) also obtained profiles of organic carbon in the cores he collected. While it would certainly be desirable to have a more extensive set of analyses, these data allow at least a preliminary assessment of the accumulation rate of organic C, N and P in the bay.

## Annual budgets

### *Organic carbon*

#### *Inputs*

The five measured rivers delivered about  $1360 \times 10^6$  moles  $\text{y}^{-1}$  of organic carbon to the bay during the time of measurement, with almost 80% in the form of DOC (Table 6). Since the flow from these rivers accounts for about 75% of the total long-term surface water drainage to the bay (Table 2), the total organic carbon input carried by rivers and streams may amount to about  $1800 \times 10^6$  moles  $\text{y}^{-1}$ .

In all of the measured rivers there was a strong positive correlation between water discharge and carbon flux (Fig. 3). The concentrations of DOC and POC were relatively constant within each river throughout the year and the annual means varied only by a factor of 1.3 and 1.75, respectively, among the rivers (Table 7).

We do not know why the concentrations of POC measured by Boucher (1991) in the Taunton River were about twice those we found in the Blackstone at similar flow rates. This was not the case with PN or PP. Because the POC flux in the Taunton appeared to be unusual, we estimated the DOC flux (unmeasured by Boucher 1991) from the measured DON flux using the mean annual DOC/DON ratio of 13.3 that we observed in the Blackstone River. This ratio varied from 11.5 to 15 in the three smaller rivers we studied.

It is possible to use the "instantaneous" flux vs. flow regressions and the average daily discharge measured by the U.S.G.S. on each day of 1983 to calculate an annual flux of organic carbon that can be compared to the annual

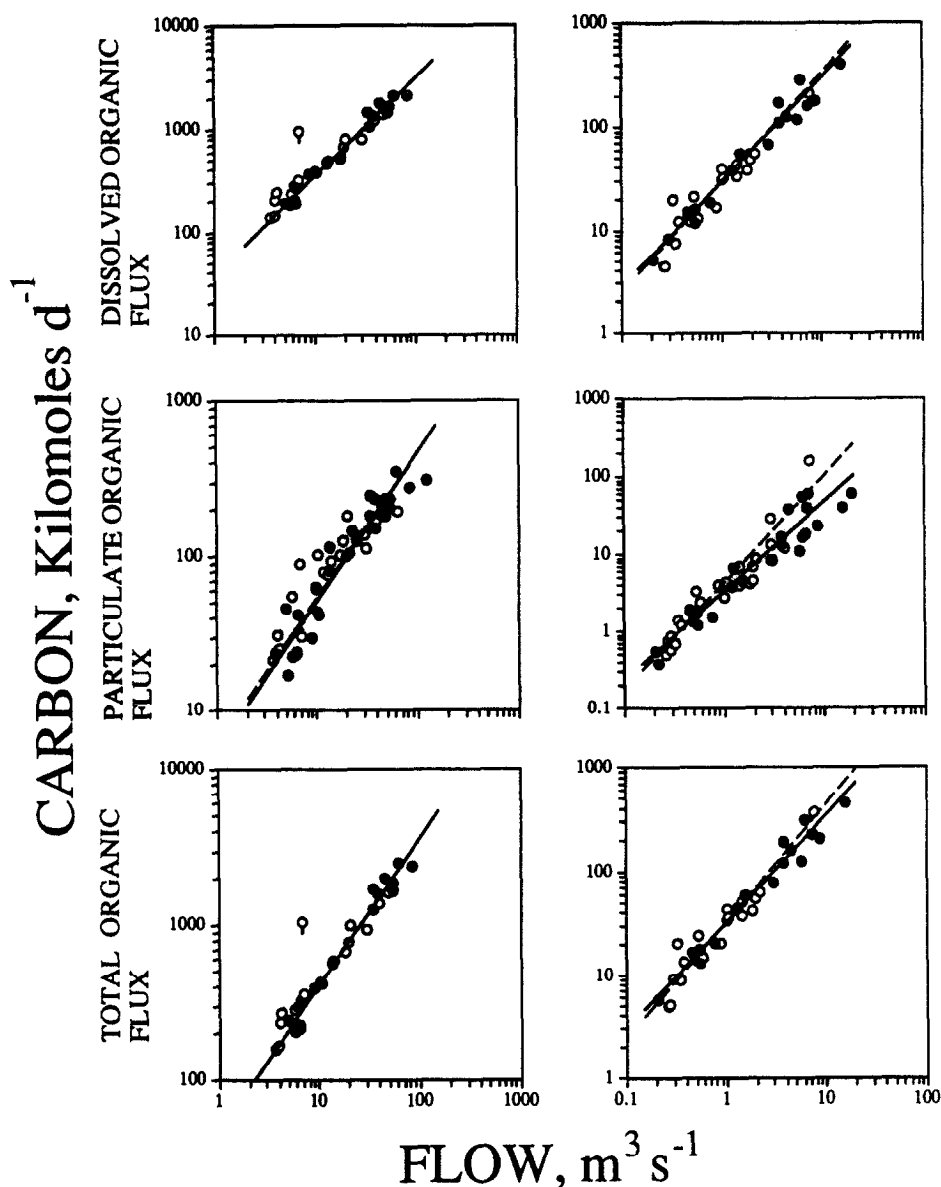


Fig. 3. Daily flux of dissolved, particulate, and total organic carbon as a function of average daily water flow in the Blackstone (solid circles) and Pawtuxet Rivers (left) and in the Woonasquatucket (solid circles) and Moshassuck Rivers (right). Values for the intercept, slope, and  $r^2$  of the log-log regression equations for DOC, PC, and TC were 1.59, 0.95, 0.97; 0.75, 0.95, 0.90; 1.66, 0.95, 0.97 for the Blackstone River (solid line) and 1.74, 0.84, 0.96; 0.83, 0.93, 0.81; 1.78, 0.86, 0.96 for the Woonasquatucket River (solid line). Regressions for the Pawtuxet River and Moshassuck River were not significantly different from the Blackstone and Woonasquatucket, respectively. Tailed points were excluded from regressions.

**Table 6.** The annual input of organic carbon to Narragansett Bay from rivers and streams. Units are  $10^6$  moles  $y^{-1}$ .

|  | DOC  | POC | Total OC |
|--|------|-----|----------|
| Blackstone River (1982–1983)           | 400  | 60  | 460      |
| Pawtuxet River (1982–1983)             | 220  | 35  | 255      |
| Woonasquatucket River (1982–1983)      | 45   | 7   | 52       |
| Moshassuck River (1982–1983)           | 15   | 5   | 20       |
| Taunton River (1988–1989) <sup>1</sup> | 400* | 174 | 574      |
|  | 1080 | 281 | 1361     |
| Unmeasured flows <sup>2</sup>          | 360  | 94  | 454      |
| Total                                  | 1440 | 375 | 1815     |

<sup>1</sup> Calculated from data of Boucher (1991).

\* Calculated from measured DON and the ratio of DOC:DON found in the Blackstone River.

<sup>2</sup> Prorated on the basis of flow from the measured rivers and streams.

**Table 7.** Concentrations of DOC and POC measured in rivers and streams entering Narragansett Bay. Units are mM.

|                            | DOC       | POC       |
|----------------------------|-----------|-----------|
| Blackstone River           |           |           |
| Range                      | 0.30–0.49 | 0.03–0.10 |
| Mean                       | 0.42      | 0.06      |
| Pawtuxet River             |           |           |
| Range                      | 0.32–0.68 | 0.04–0.12 |
| Mean                       | 0.51      | 0.07      |
| Woonasquatucket River      |           |           |
| Range                      | 0.24–0.55 | 0.02–0.10 |
| Mean                       | 0.33      | 0.04      |
| Moshassuck River           |           |           |
| Range                      | 0.18–0.71 | 0.02–0.25 |
| Mean                       | 0.32      | 0.05      |
| Taunton River <sup>1</sup> |           |           |
| Range                      |           | 0.07–0.21 |
| Mean                       |           | 0.13      |

<sup>1</sup> Boucher (1991).

flux calculated using Beale's flow-weighted estimate. After correcting for the bias introduced by the use of log-log regressions (Ferguson 1986), the total

organic carbon flux from the four rivers we measured amounted to about  $1000 \times 10^6$  moles when calculated in this way compared to about  $790 \times 10^6$  moles using Beale's technique. We do not know which estimate is more nearly "correct", but our regressions produce a carbon flux that is virtually identical to that predicted by the regression of annual organic carbon flux on annual water discharge in 11 much larger rivers around the world (Schlesinger & Melack 1981). One advantage of the regression is that it can be used to estimate fluxes in years with different patterns of water discharge. For example, 1983 was a relatively wet year in which total fresh water flow averaged  $135 \text{ m}^3 \text{ s}^{-1}$  compared to the mean for 1963–1984 of  $91 \text{ m}^3 \text{ s}^{-1}$  (Pilson 1989). We have applied the regressions measured in 1983 to the daily discharges of a dry year (1980, discharge =  $62 \text{ m}^3 \text{ s}^{-1}$ ) and calculated an annual flux of  $740 \times 10^6$  moles from the same four rivers, or about 75% of the wet year regression value.

The flux of organic carbon from the three sewage treatment plants we measured amounted to about  $300 \times 10^6$  moles in 1983 (Table 8). Approximately half (55%) was in the form of DOC, though this varied markedly among the plants. Almost 90% of the POC was released by the Fields Point facility, which was in poor repair during the time of our measurements (Table 8). The concentrations of DOC in the effluents from the three plants were reasonably similar, while the POC concentrations in Fields Point effluent were much higher (Table 9).

It is probably appropriate to attempt to correct for the poor performance of the Fields Point facility before extrapolating these data to other treatment plants around the bay. If we assume that a more typical discharge would contain a POC load equal to 25% of the DOC released (Table 8), then the "corrected" discharge from Fields Point would be reduced to  $25 \times 10^6$  moles of POC and the "corrected" total organic carbon discharge for all three plants would become about  $200 \times 10^6$  moles  $\text{y}^{-1}$ . Since these facilities account for 84% of the total sewage effluent discharged directly to the bay (Table 5), the total input of organic carbon from treatment plants may have been about  $330 \times 10^6$  moles in 1983. If the Fields Point plant had been operating more effectively, the total might have been closer to  $240 \times 10^6$  moles.

The major remaining input of organic carbon is from the photosynthetic activity of the phytoplankton. Unfortunately, the data base for this term is surprisingly small. Water samples collected over an annual cycle near the middle of the West Passage and incubated with  $^{14}\text{C}$  on land in a light gradient box provided a value of  $310 \text{ g C m}^{-2} \text{ y}^{-1}$  (Furnas et al. 1976). Three years of  $^{14}\text{C}$  uptake measurements using water collected from the lower West Passage and incubated in a 5 m deep, 2 m diameter tank of bay water at the Marine Ecosystems Research Laboratory (MERL) resulted in values of 250, 165,

*Table 8.* The annual input of organic carbon to Narragansett Bay from sewage treatment plants. Units are  $10^6$  moles  $y^{-1}$ .

|                    | DOC | POC | Total OC | POC/DOC |
|--------------------|-----|-----|----------|---------|
| Fields Point       | 100 | 120 | 220      | 1.20    |
| Bucklin Point      | 50  | 12  | 62       | 0.24    |
| East Providence    | 9   | 2   | 11       | 0.22    |
| Unmeasured plants  | ~30 | ~7  | 37       |         |
| Total <sup>1</sup> | 189 | 141 | 330      |         |

<sup>1</sup> Totals corrected for excess POC discharged at Fields Point during 1983: DOC = 189, POC = 46, TOC =  $235 \times 10^6$  moles  $y^{-1}$ .

*Table 9.* Concentrations of DOC and POC measured in sewage treatment plant effluents entering Narragansett Bay. Units are mM.

|                 | DOC      | POC       |
|-----------------|----------|-----------|
| Fields Point    |          |           |
| Range           | 0.70–3.5 | 0.27–8.6  |
| Mean            | 1.5      | 1.3       |
| Bucklin Point   |          |           |
| Range           | 0.74–2.9 | 0.19–0.81 |
| Mean            | 1.8      | 0.42      |
| East Providence |          |           |
| Range           | 0.51–1.7 | 0.11–0.46 |
| Mean            | 0.92     | 0.22      |

and  $150 \text{ g C m}^{-2} \text{ y}^{-1}$  (Keller 1988). However, vertical light attenuation coefficients in the MERL tanks are higher than in the bay ( $\sim 1 \text{ m}^{-1}$  vs.  $0.4 \text{ m}^{-1}$ ), and these production values may therefore be underestimates of rates in the field (Fig. 4). Light and dark bottle  $\text{O}_2$  measurements of net daytime production by the plankton community suggest that production in the Providence River may be almost twice that in the bay proper (Oviatt et al. 1981). Since primary production on the order of  $300 \text{ g C m}^{-2} \text{ y}^{-1}$  converts to a total organic carbon input to the bay of  $8200 \times 10^6$  moles  $\text{C y}^{-1}$ , it is clear that this source is considerably larger than the  $1800 \times 10^6$  moles  $\text{C y}^{-1}$  from rivers and  $330 \times 10^6$  moles  $\text{C y}^{-1}$  from direct sewage discharges (Tables 6 and 8).



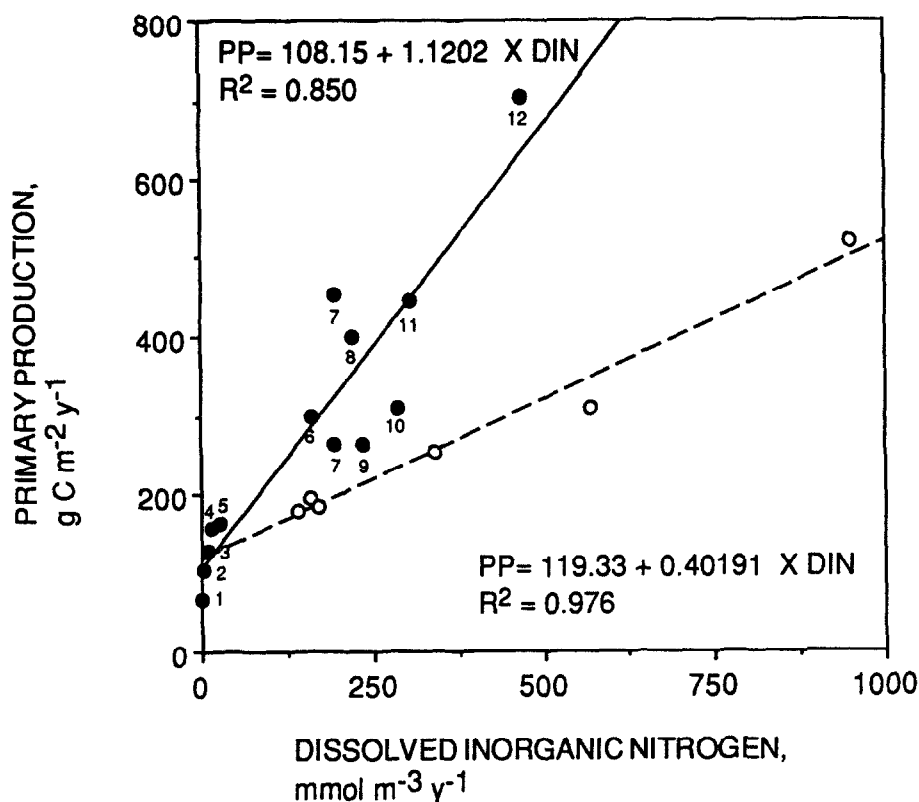


Fig. 4. Primary production ( $^{14}\text{C}$  uptake) by phytoplankton in 12 marine and estuarine systems (solid points and line) and in three control and three fertilized MERL mesocosms (open points and broken line) as a function of the volume-specific input rate of dissolved inorganic nitrogen. See text. Data sources and assumptions are given in Nixon (1992). Natural systems include (1) Sargasso Sea, (2) North Central Pacific Gyre, (3) Kaneohe Bay post sewage diversion, (4) Baltic Sea, (5) Kaneohe Bay pre sewage diversion, (6) New York Shelf, (7) Georges Bank range, (8), Peru upwelling, (9) Tomales Bay, (10) Potomac estuary, (11) Upper Chesapeake Bay, (12) Patapsco River estuary.

We believe it is possible to estimate the bay-wide average carbon fixation rate more closely than the currently available measurements allow by taking advantage of the empirical relationship between the volume-specific rate of input of reactive nitrogen and primary production by phytoplankton in a wide variety of other marine ecosystems (Nixon 1992). Our inventory of reactive nitrogen inputs will be developed in detail later in this paper. Briefly, we include DIN from direct atmospheric deposition, rivers, sewage, urban runoff, and offshore, and assume that all of the DON in direct sewage discharges and 25% of the DON in rivers is also used directly by the phytoplankton (e.g., urea) or converted relatively rapidly to DIN. These assumptions are consistent with the preliminary results of ongoing research on DON in estuaries (S.

Seitzinger, Rutgers University, personal communication). As described later, the total DIN input to a bay volume of  $2724 \times 10^6 \text{ m}^3$  (Pilson 1985a) amounts to  $210 \text{ mmol DIN m}^{-3} \text{ y}^{-1}$ . If the DON inputs described above also contribute to the metabolism of the bay, the reactive N input is increased to  $235 \text{ mmol m}^{-3} \text{ y}^{-1}$ . A regression relating primary production to reactive nitrogen input in 12 marine systems suggests that these levels of N input should result in an average carbon fixation of  $340\text{--}370 \text{ g C m}^{-2} \text{ y}^{-1}$ , respectively (Fig. 4).

Based on the nitrogen input to the bay, the data of Furnas et al. (1976) and Oviatt et al. (1981), and considering that Keller's (1988) measurements in the MERL tanks probably underestimated rates in the field (Fig. 4), we adopted a value of  $350 \text{ g C m}^{-2} \text{ y}^{-1}$  as a working estimate of the bay-wide average primary production. This is equivalent to an input of  $9600 \times 10^6 \text{ moles C y}^{-1}$ . The total organic carbon input to Narragansett Bay thus appears to be about  $11650 \times 10^6 \text{ moles y}^{-1}$ , 80% of which is fixed within the bay.

### *Outputs*

The net exchange of  $\text{CO}_2$  between Narragansett Bay and the atmosphere or at the bay mouth has never been measured, nor is there any other direct evidence available to establish if the bay is net autotrophic or heterotrophic. Preliminary calculations based on nutrient stoichiometry suggested that the bay exports organic carbon to the offshore amounting to almost  $2000 \times 10^6 \text{ moles y}^{-1}$  (Nixon and Pilson 1984). After developing the nitrogen and phosphorus budgets in later sections it will be possible to recalculate that estimate using more complete data. At this point, the only unambiguous loss of organic carbon that we can evaluate is the harvest of clams. Since the carbon content of clam meats is between 5 and 10% of their fresh weight, the harvest of  $1.75 \times 10^6 \text{ kg y}^{-1}$  represents a removal of some  $7\text{--}14 \times 10^6 \text{ moles of carbon}$ .

### *Changes within the bay*

It is worth describing our estimate of the amount of organic carbon buried with the accumulating sediments in the bay in some detail, because much of what is developed here will also be used for nitrogen and phosphorus burial. We began by assuming that virtually all of the sediment is accumulating in depositional areas characterized by fine-grained sediments (silts and clays). The grain-size distribution of surficial sediments in the bay was described by McMaster (1960) on the basis of hundreds of cores. Those data have now been analyzed using the ARC/INFO software of the R. I. Geographical Information System. The distribution of fine-grained depositional areas has been mapped (Fig. 5), and the extent of depositional area within each region of the bay calculated (Table 10). McMaster (1960) was unable to sample the

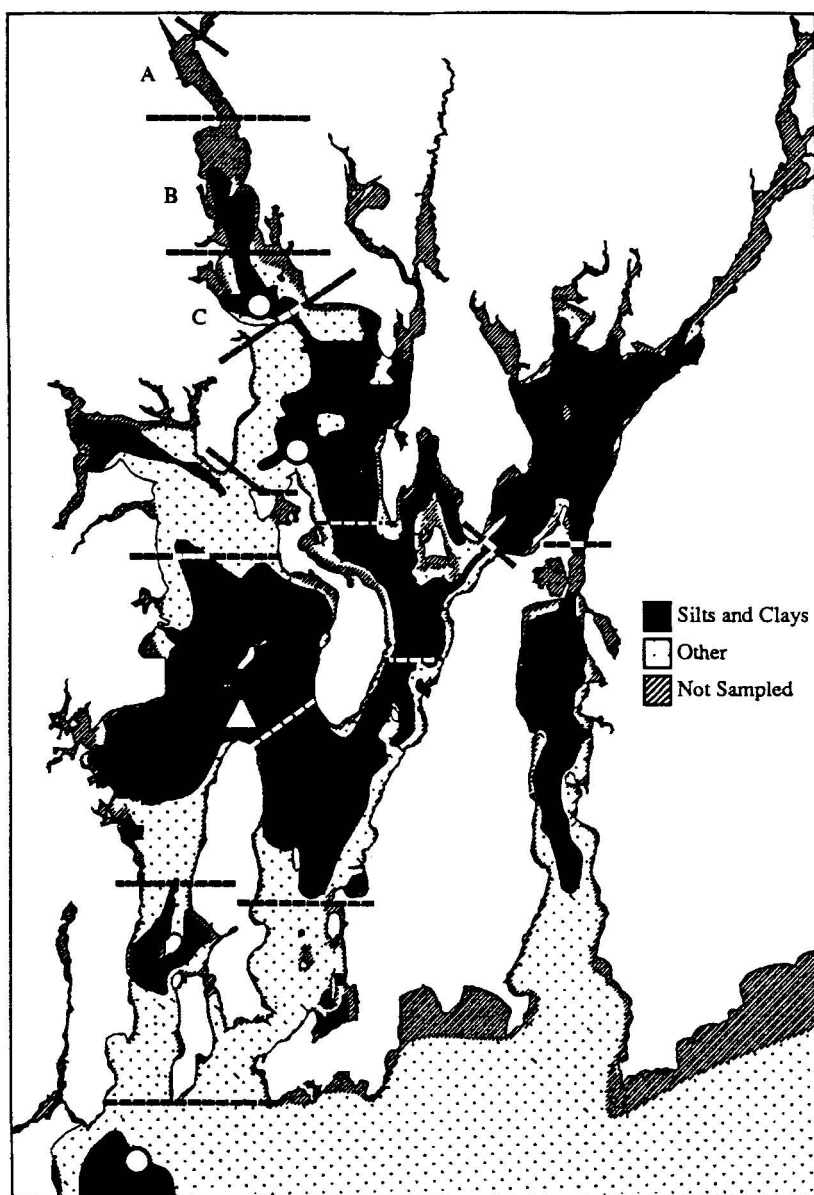


Fig. 5. The distribution of fine grained (silt and clay) sediments in Narragansett Bay. Contours were generated by the Rhode Island Geographical Information System using ARC/INFO software and data from hundreds of cores analyzed by McMaster (1960). Broken lines are the boundaries of regional elements used in Table 10: A is the Fox Point Reach of the Providence River, B is the Sabin Point Reach, C is the Nyatt Point Reach. Open circles show sites where Seitzinger et al. (1984) measured denitrification; open triangle is the area from which sediments were collected for use in the MERL mesocosm experiments discussed in text and for the denitrification measurements of Nowicki (1994).

Table 10. Estimates of the area of fine-grained sediments, the rate of sediment deposition, and the total mass of sediment accumulating in various regions of Narragansett Bay (see Figs. 1 and 5).

|                                 | Total area<br>km <sup>2</sup> | Depositional<br>area km <sup>2</sup> | Deposition rate<br>mg cm <sup>-2</sup> y <sup>-1</sup> | Total deposition<br>kg y <sup>-1</sup> × 10 <sup>6</sup> |
|---------------------------------|-------------------------------|--------------------------------------|--|--|
| Seekonk River <sup>a</sup>      | 2.8                           | 2.5                                  | 510 <sup>d</sup>                                       | 12.8   |
| Providence River <sup>a</sup>   |                               |                                      |  |  |
| Fox Point Reach                 | 3.0                           | 2.7                                  | 720 <sup>d</sup>                                       | 19.4   |
| Sabin Point Reach               | 8.5                           | 7.7                                  | 240 <sup>d</sup>                                       | 18.5   |
| Nyatt Point Reach               | 9.8                           | 8.8                                  | 240 <sup>d</sup>                                       | 21.1   |
| Providence River Total          | 21.3                          | 19.2                                 |  | 59.0   |
| Upper Bay <sup>b</sup>          | 49.5                          | 30.7                                 | 135 <sup>c</sup> –230 <sup>d</sup>                     | 41.4–70.6  |
| Greenwich Bay <sup>b</sup>      | 30.6                          | 11.8                                 | 135 <sup>c</sup> –230 <sup>d</sup>                     | 15.9–27.1  |
| Upper West Passage <sup>b</sup> | 63.0                          | 50.1                                 | 10 <sup>c</sup> –225 <sup>d</sup>                      | 5.0–113  |
| Lower West Passage <sup>b</sup> | 20.6                          | 7.5                                  | 7 <sup>c</sup>   | 0.5  |
| Upper East Passage <sup>b</sup> | 26.2                          | 18.8                                 | 150 <sup>c</sup>                                       | 28.2   |
| Mid East Passage <sup>b</sup>   | 39.4                          | 26.6                                 | 100 <sup>c</sup>                                       | 26.6   |
| Lower East Passage <sup>b</sup> | 24.5                          | 5.3                                  | 100 <sup>c</sup>                                       | 5.3  |
| Mount Hope Bay <sup>c</sup>     | 49.2                          | 45.1                                 | 34   | 15.3   |
|                                 |                               |                                      |  | 210–358  |

<sup>a</sup> Areas from Chinman and Nixon (1985).

<sup>b</sup> Regions defined by Kremer and Nixon (1978); areas calculated by ARC/INFO system of the R. I. Geographical Information System. The Greenwich Bay region includes a portion of the Upper West Passage.

<sup>c</sup> Area from Pilson (1985a); sediment input from the Taunton River calculated as described in text.

<sup>d</sup> From Corbin (1989); Fox Point Reach is the average of cores at Fox Point and Fields Point, the boundaries of the reach.

<sup>e</sup> Santschi et al. (1984).

Seekonk River or the shallower coves and edges of the bay, and we have assumed that 90% of the unclassified area in each region is depositional.

We next assigned a sediment deposition rate to each region on the basis of the “dated” cores described by Santschi et al. (1984) and Corbin (1989) (Table 10). Multiplying the deposition rate per unit area from the cores by the depositional area in each region provided a total sediment accumulation rate for each region (Table 10). Unfortunately, measurements of deposition rates have not been reported for most of the East Passage or for Mt. Hope Bay. Moreover, in regions where several cores have been analyzed there is little agreement between the deposition rates calculated by Santschi et al.

(1984) and those reported by Corbin (1989) (Table 10). At this time, we see no alternative but to use both estimates in our calculations and to hope that the range will highlight the uncertainty in all burial calculations. In areas of Narragansett Bay proper where no core results have been published, we used the deposition estimates of Santschi et al. (1984), while recognizing that their values are low compared to those of Corbin (1989).

Lacking any core data or published deposition estimates for Mt. Hope Bay, we calculated the potential delivery of sediment to that region from the Taunton River using Milliman and Syvitski's (1992) regression relating riverine sediment flux to watershed area for coastal plain rivers around the world. We then assumed that all of the calculated  $15.3 \times 10^6 \text{ kg y}^{-1}$  of sediment was retained in Mt. Hope Bay. This may be an overestimate because the regression value is almost four times greater than the 1989 discharge of inorganic sediment from the Taunton River that we calculated from the data of Boucher (1991). Her study was not designed to measure the sediment discharge from the river, however, and her monthly sampling schedule missed several peak flows. The winter of 1989 was also very dry (mean January–May discharge = 47% of the 27 year mean), while the summer was very wet (Boucher 1991). The Taunton River was also sampled near the surface, and sediment concentrations may have been higher near the bottom.

As a final comparison, we used Milliman and Syvitski's (1992) regressions to calculate the sediment flux from each of the rivers flowing into Narragansett Bay (Table 2). We applied their equation for coastal plain rivers to all flows except the Blackstone, which rises in higher country northwest of the bay and thus qualifies as a lowland (100–500 m headwater) river. The total sediment input of  $140 \times 10^6 \text{ kg y}^{-1}$  calculated in this way is about 40–65% of the core-based estimate given in Table 10. However, considering that Milliman and Syvitski's (1992) regressions were derived from a global data set emphasizing much larger rivers and that the calculated sediment flux is quite sensitive to the elevation of a river's headwaters, this is probably reasonable agreement. Moreover, the variability in the core-based sedimentation rates and the lack of coverage in many areas of the bay would support the view that the sediment input calculated from the regressions is at least as credible as the estimates summarized in Table 10. As a practical matter, we can only emphasize that there is considerable uncertainty surrounding the estimates of sediment deposition in the bay and that the higher end of the range given in Table 10 is likely to be an overestimate. We conclude this because the regressions predict a lower sediment input and yet they describe sediment fluxes in rivers without dams. Most of the rivers entering Narragansett Bay have numerous dams which should trap sediment and thus lower the sediment flux compared to predictions from the regressions.

The remaining task was to establish the concentrations of organic carbon associated with the accreting sediments (Table 11) and the total accumulation of carbon in each region. The latter was obtained by multiplying the concentration data by the appropriate mass of accumulating sediment from Table 10. The result suggests that some  $575\text{--}880 \times 10^6$  moles of organic carbon are being sequestered in the sediments of the bay each year (Table 11).

### *The annual budget*

Photosynthetic fixation by phytoplankton is clearly the most important pathway by which organic carbon enters Narragansett Bay, though direct anthropogenic discharges and land drainage add an amount equal to about 20% of the primary production (Table 12). The major fishery removes less than 0.2% of the primary production, and burial or storage within the bay accounts only for about 5–10% of the total organic carbon input. Major loss or export terms are clearly missing from the budget. Our best hope for moving toward some reconciliation of inputs and outputs is to use a stoichiometric model to attempt to calculate the organic carbon exported from the bay (Nixon & Pilson 1984), but that exercise requires a complete inventory of nitrogen and phosphorus inputs.

### *Nitrogen*

#### *Inputs*

Recent measurements of nitrogen deposition from the atmosphere on Prudence Island, in the middle of the bay (Fig. 1), showed that about  $30 \times 10^6$  moles  $y^{-1}$  are deposited directly on the water surface. About 30% of the total is added in the form of dry deposition (Table 13).

The flux of total nitrogen in the five major rivers where concentration measurements were made amounted to  $325 \times 10^6$  moles  $y^{-1}$ . About 73% of the total was DIN, 24% was DON, and 3% was PN (Table 14). This distribution was remarkably consistent among all of the rivers. If these results are simply prorated to the remaining 25% of the total fresh water drainage in which no measurements were made, the total nitrogen flux is increased to  $435 \times 10^6$  moles  $y^{-1}$ . While this was the procedure followed for organic carbon, it is possible to refine this extrapolation in the case of nitrogen.

At least  $316 \text{ km}^2$  of land in cities and towns adjacent to the bay are developed (Table 4). These built-up urban and suburban areas comprise about 70% of the  $438 \text{ km}^2$  that Ries (1990) called "ungauged areas adjacent to bay". He calculated a long-term fresh water runoff from the ungauged coastal areas of  $11.9 \text{ m}^3 \text{ s}^{-1}$ . Assuming that runoff from the built-up areas may be 50–75% of precipitation (Schueler 1987), storm water runoff could account for 6–9  $\text{m}^3 \text{ s}^{-1}$  of this total.

*Table 11.* Estimates of the organic carbon composition of sediments accumulating in various regions of Narragansett Bay and the total rate of storage of organic carbon in depositional areas of the bay.

|                                 | Organic carbon<br>% dry weight <sup>a</sup> | Organic carbon<br>accumulation $\text{kg y}^{-1} \times 10^6$ |
|---------------------------------|---|---|
| Seekonk River <sup>b</sup>      | ~10   | 1.3   |
| Providence River <sup>b</sup>   |   |   |
| Fox Point Reach                 | ~8  | 1.6   |
| Sabin Point Reach               | ~5  | 0.9   |
| Nyatt Point Reach               | ~2.5  | 0.5   |
| Upper Bay <sup>b,c</sup>        | 2.5–3.0                                     | 1.0–2.1   |
| Greenwich Bay <sup>b</sup>      | 1.5–2.0                                     | 0.2–0.5   |
| Upper West Passage <sup>d</sup> | 1.7–1.9                                     | 0.09–2.1  |
| Lower West Passage <sup>c</sup> | 1   | 0.005   |
| Upper East Passage <sup>e</sup> | 2   | 0.6   |
| Mid East Passage <sup>c</sup>   | 1.5   | 0.4   |
| Lower East Passage <sup>c</sup> | 1   | 0.05  |
| Mount Hope Bay <sup>c</sup>     | 2–3   | 0.3–0.5   |
| Total                           |   | 6.9–10.6  |

<sup>a</sup> Below zone of bioturbation that enriches the surface 10–20 cm.

<sup>b</sup> Corbin (1989).

<sup>c</sup> Nixon and Pilson (1984).

<sup>d</sup> Frithsen et al. (1985).

<sup>e</sup> Estimated from similar locations in Narragansett Bay. Analyses of surficial (top 0.5 cm) sediments from many locations in the bay suggest that the concentrations of organic C, N, and P on the sediments are largely a function of distance from the head of the bay (King et al. 1991).

We multiplied the DIN runoff coefficients for urban areas around the bay (Table 3) by the appropriate entry in the land use inventory in urban areas adjacent to the bay (Table 4) and summed the results to calculate the total potential DIN flux from this source. We used the ratio of total nitrogen to DIN in runoff from older urban areas (1.36) and from new suburban sites (2.70) to estimate the total N in runoff from cities around the Providence River and upper bay, Fall River, and Newport and from East Greenwich and North Kingstown, respectively (Schueler 1987). The result suggests that storm water runoff directly to the bay may add about  $17 \times 10^6$  moles of DIN  $\text{y}^{-1}$  and an additional  $20 \times 10^6$  moles  $\text{y}^{-1}$  of organic N.

If urban storm water of  $6\text{--}9 \text{ m}^3 \text{ s}^{-1}$  is subtracted from the total freshwater flow of  $24.7 \text{ m}^3 \text{ s}^{-1}$  which lacked nitrogen concentration measurements (Table 2), the remaining  $15.7\text{--}18.7 \text{ m}^3 \text{ s}^{-1}$  accounts for 17–20% of the total land

*Table 12.* Current assessment of the annual mass balance of organic carbon in Narragansett Bay. See Tables 6, 8, and 11. Units are  $10^6$  moles  $y^{-1}$

|                                      | DOC  | POC     | Total   |
|--------------------------------------|------|---------|---------|
| <b>Inputs</b>                        |      |         |         |
| Rivers and streams                   | 1440 | 375     | 1815    |
| Sewage treatment plants <sup>a</sup> | 190  | 140     | 330     |
|                                      | 190  | 45      | 235     |
| Primary production                   | ?    | 9600    | 9600    |
|                                      |      |         | 11650   |
| <b>Outputs</b>                       |      |         |         |
| Export to offshore                   | ?    | ?       | ?       |
| Hard clam harvest                    | —    | 7–14    | 7–14    |
| Total system respiration ( $CO_2$ )  |      |         | ?       |
| <b>Changes in storage</b>            |      |         |         |
| Accumulation in sediments            | —    | 575–880 | 575–880 |

<sup>a</sup> Lower values corrected for malfunction of Fields Point plant.

*Table 13.* The direct deposition of nitrogen from the atmosphere onto Narragansett Bay (Fraher 1991).

|                       | $mmol\ m^{-2}\ y^{-1}$ | $moles\ y^{-1} \times 10^6$ |
|-----------------------|------------------------|-----------------------------|
| <b>Wet deposition</b> |                        |                             |
| Nitrate               | 29                     | 9.5                         |
| Range                 | 27–31                  |                             |
| Ammonium              | 17                     | 5.6                         |
| Range                 | 13–21                  |                             |
| DON <sup>2</sup>      | 17                     | 5.6                         |
| Range                 | 16–18                  |                             |
| <b>Dry deposition</b> |                        |                             |
| Vapor                 | 18                     | 5.9                         |
| Range                 | 12–25                  |                             |
| Aerosol               | 10                     | 3.3                         |
| Range                 | 5–15                   |                             |
| Total                 | 91                     | 29.9                        |
| Range                 | 73–110                 | 23.9–36.1                   |

<sup>a</sup> From Nowicki and Oviatt (1990) regression relating DON to  $NO_3$ .



*Table 14.* The annual input of nitrogen to Narragansett Bay from rivers and streams. Units are  $10^6$  moles  $y^{-1}$ .

|                               | NO <sub>3</sub> | NO <sub>2</sub> | NH <sub>4</sub> | DON | PN  | Total N |
|-------------------------------|-----------------|-----------------|-----------------|-----|-----|---------|
| Blackstone River              | 60              | 1.4             | 35              | 30  | 5   | 131     |
| Pawtuxet River                | 20              | 1.0             | 25              | 15  | 3   | 64      |
| Woonasquatucket River         | 4.9             | 0.05            | 1.7             | 3   | 0.6 | 10      |
| Moshassuck River              | 2.5             | 0.1             | 0.8             | 1.3 | 0.3 | 5       |
| Taunton River <sup>1</sup>    | 55              | 1.1             | 30              | 30  | 1.0 | 117     |
|                               | 141             | 3.6             | 93              | 79  | 10  | 327     |
| Unmeasured flows <sup>2</sup> | 31              | 0.8             | 20              | 17  | 2.2 | 72      |
|                               | 173             | 4.4             | 113             | 196 | 12  | 399     |

<sup>1</sup> Calculated from data of Boucher (1991) collected in 1988–1989. Other rivers measured in 1982–1983.

<sup>2</sup> Prorated on the basis of flow from the measured rivers and streams.

drainage. If the N flux in the measured rivers is prorated to the middle of this flow range, it could provide almost  $75 \times 10^6$  moles  $N y^{-1}$ . The total nitrogen flux in rivers and streams would be  $400 \times 10^6$  moles  $y^{-1}$ , and direct urban runoff would add  $40 \times 10^6$  moles  $y^{-1}$ .

The fluxes of NO<sub>2</sub> plus NO<sub>3</sub>, total dissolved N, and total N were strongly correlated with flow in the rivers we measured (Fig. 6). In the same way we analyzed organic carbon, we used these regressions with daily discharge measurements from 1983 to calculate annual fluxes for comparison with those obtained using the unbiased flow-weighted estimate. The regression technique produced values that were 1.05, 1.24, and 1.24 times greater than the flow-weighted estimates of NO<sub>2</sub> plus NO<sub>3</sub>, total dissolved N, and total N, respectively. Using the regression technique to compare fluxes in different years suggested that total nitrogen input to the bay from rivers in a dry year (1980) might be only 60% of that in a wet year (1983).

The only remaining source of nitrogen is the direct discharge of sewage treatment plants. Our annual cycle of measurements in three of the four largest plants showed a discharge of about  $120 \times 10^6$  moles  $y^{-1}$ , with almost 75% of the nitrogen in the form of NH<sub>4</sub> (Table 15). Particulate N made up only 3–6% of the total N discharge among the three plants, so that there appears to be no need to assess the impact of the poor performance of the Fields Point facility as there was for carbon.

Four measurements of the Fields Point, Bucklin Point, and East Providence plants during 1985–1986 (Pilson & Hunt 1989) gave estimates of an annual N

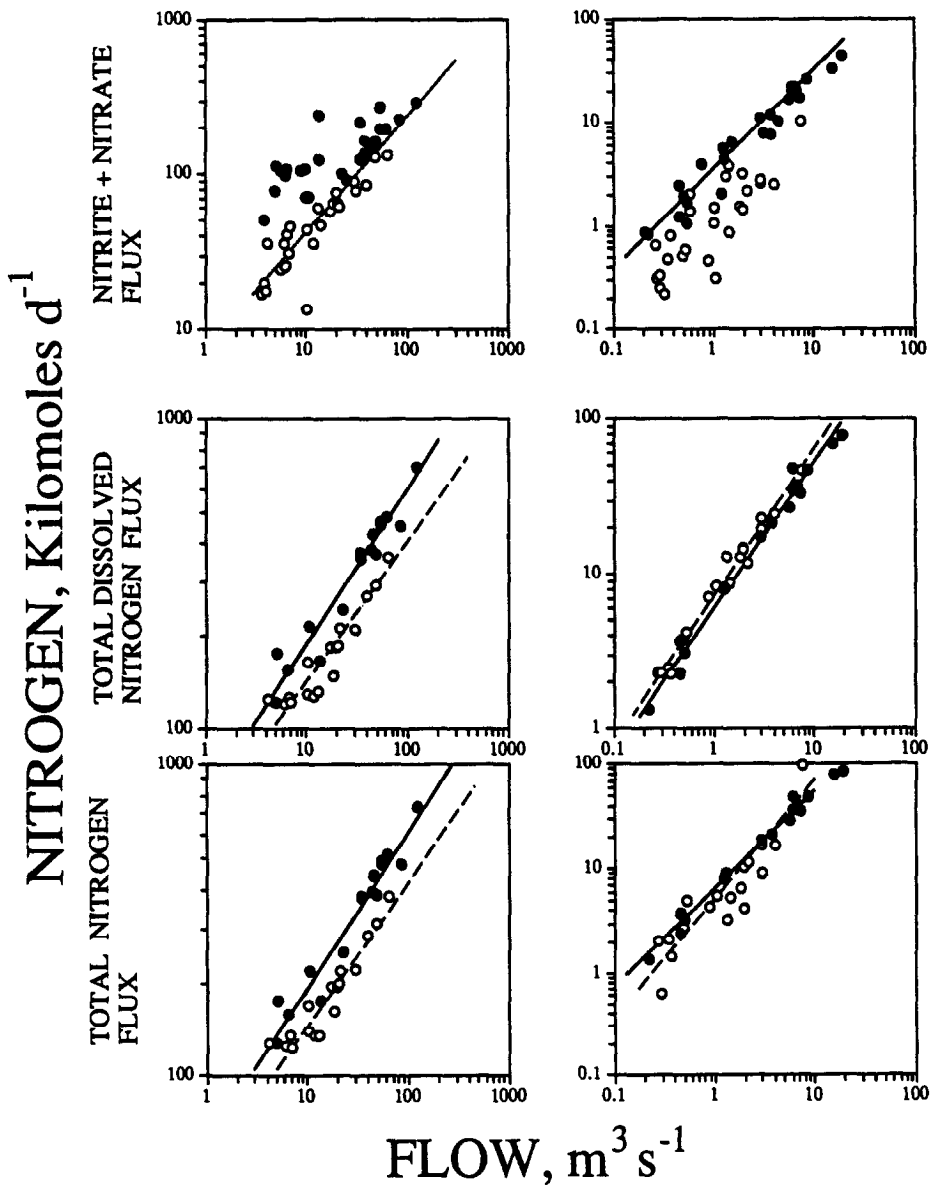


Fig. 6. Daily flux of various forms of nitrogen as a function of average daily water flow in the Blackstone (solid circles) and Pawtuxet Rivers (left) and in the Woonasquatucket (solid circles) and Moshassuck Rivers (right). Values for the intercept, slope and  $r^2$  of the log-log regression equations for nitrite plus nitrate, total dissolved nitrogen, and total nitrogen were: no significant regression; 1.77, 0.50, 0.93; 1.78, 0.51, 0.94 for the Blackstone River (solid line), 0.85, 0.75, 0.73; 1.70, 0.45, 0.86; 1.71, 0.46, 0.88 for the Pawtuxet River, 0.51, 0.93, 0.95; 0.78, 0.94, 0.99; 0.80, 0.94, 0.99 for the Woonasquatucket River (solid line), and no significant regression; 0.86, 0.95, 0.98; 0.66, 1.14, 0.81 for the Moshassuck River.

*Table 15.* The annual input of nitrogen to Narragansett Bay from the direct discharge of sewage treatment plants. Units are  $10^6$  moles  $y^{-1}$ .

|   | $NO_2 + NO_3$ | $NH_4$     | DON       | PN        | Total N    |
|---|---------------|------------|-----------|-----------|------------|
| <b>Measured biweekly (1983)</b>                 |               |            |           |           |            |
| Fields Point                                    | 3.0           | 60         | 15        | 5.0       | 83         |
| Bucklin Point                                   | 0.3           | 20         | 4.0       | 1.4       | 26         |
| East Providence                                 | 0.8           | 10         | 1.3       | 0.3       | 12         |
|   | 4.1           | 90         | 20        | 6.7       | 121        |
| <b>Measured 3–4 times (1985–86)<sup>a</sup></b> |               |            |           |           |            |
| East Greenwich                                  |               |            |           |           | 2.1        |
| Quonset   |               |            |           |           | 1.0        |
| Warren  |               |            |           |           | 2.4        |
| Bristol   |               |            |           |           | 5.2        |
| Jamestown                                       |               |            |           |           | 0.2        |
| Newport   |               |            |           |           | 20         |
| Fall River                                      |               |            |           |           | 31         |
|   | 2.1*          | 46*        | 10*       | ~3.4*     | 62         |
| <b>Total</b>                                    | <b>6.2</b>    | <b>136</b> | <b>30</b> | <b>10</b> | <b>183</b> |

\* Calculated from total N input assuming the same relative composition as the plants where measurements were obtained.

<sup>a</sup> Pilson & Hunt (1989). Monthly measurements of DIN fluxes in 1992 gave values of 0.98, 1.6, 1.9, 4.1, 0.3, and 9.2, respectively, for the smaller R. I. treatment plants (Save the Bay 1992).

flux that was 113%, 83%, and 54%, respectively, of the values we measured with a much more intensive sampling program three years earlier.

### *Outputs*

Narragansett Bay was the first system in which denitrification in the sediments was measured directly over an annual cycle by observing the fluxes of  $N_2$  and  $N_2O$  from intact, unamended cores (Seitzinger et al. 1984). The results of that study suggested that approximately  $520 \text{ mmol N m}^{-2} \text{ y}^{-1}$  were removed from the bay through denitrification, a loss amounting to  $170 \times 10^6$  moles  $y^{-1}$  if the average rate is applied to the entire bay. Two of the three sites measured were in areas of sandy sediment and one was in a silt/clay sediment. No significant differences were found between sites. Less than 1% of the bay bottom consists of gravel and other material coarser than sand (McMaster 1960), so a bay-wide extrapolation may be appropriate. If the rate of  $520 \text{ mmol m}^{-2} \text{ y}^{-1}$  is only applied to the fine grained and more organic rich

depositional area in the bay (Table 10), the total N removed is reduced to  $115 \times 10^6$  moles  $y^{-1}$ .

A more recent estimate of denitrification in the bay arrived at an annual average of  $385 \text{ mmol m}^{-2} y^{-1}$  (Nowicki 1994), which would result in a loss of  $125 \times 10^6$  moles  $y^{-1}$  if applied to the whole system or  $85 \times 10^6$  moles  $y^{-1}$  if restricted to the fine-grained sediments. If we accept the extremes of these two studies as limits, denitrification removes  $85\text{--}170 \times 10^6$  moles N  $y^{-1}$  from the bay.

The only remaining N loss we can quantify by direct measurement is the removal in the hard clam fishery. *Mercenaria mercenaria* tissue contains about 2.7% N on a fresh weight basis (Vinogradov 1953), so the annual harvest of  $1.75 \times 10^6$  kg converts to  $3.4 \times 10^6$  moles N  $y^{-1}$ .

#### *Changes within the bay*

Since there do not appear to be any recent secular trends in the concentrations of nitrogen in the water column (Pilson 1985b; Hinga et al. 1989), we were left to assess the burial of nitrogen with the accumulating sediment in the bay (Table 10). There have been fewer measurements of nitrogen concentrations than carbon concentrations on the sediments below the zone of bioturbation, so we chose to apply a reasonable range of the C/N ratio to estimate nitrogen burial from the carbon burial calculations (Table 11). Sediments accumulating in the Upper Bay have an organic C to N molar ratio of about 12–14 (Nixon & Pilson 1984) while those in the mid bay region have a ratio of 11–12 (Frithsen et al. 1985). A core from the lower West Passage showed a C/N ratio of about 15–20 below 15–20 cm (Nixon & Pilson 1984). Extrapolating from these few measurements requires caution, and we have assumed a C/N (molar) range for the various regions of the bay as follows: Seekonk and Providence River estuary = 8–12; all of the remaining areas except the lower West and East Passages = 10–15; lower passages = 15–20. If these ranges are applied to the carbon burial estimates (Table 11), the result suggests that some  $45\text{--}100 \times 10^6$  moles N  $y^{-1}$  are accumulating in the bay.

#### *The annual budget*

Rivers are the major pathway by which nitrogen enters Narragansett Bay from land and atmosphere, though in this urban watershed much of the nitrogen carried by the rivers has been added by upstream sewage treatment plants and other anthropogenic sources. Over 70% of the nitrogen entering the bay is in the form of DIN, with DON accounting for about 20% (Table 16). The DIN is partitioned almost equally between  $\text{NH}_4$  and the oxidized forms. The direct discharge of sewage treatment plants adjacent to the bay provides almost 30% of the annual nitrogen input, and almost 75% of the effluent nitrogen is in the form of  $\text{NH}_4$ .

**Table 16.** Current assessment of the annual mass balance of nitrogen in Narragansett Bay. See Tables 13, 14, and 15. Units are  $10^6$  moles  $y^{-1}$ .

|                               | NO <sub>2</sub> + NO <sub>3</sub> | NH <sub>4</sub> | DIN | DON | PN | Total   |
|-------------------------------|-----------------------------------|-----------------|-----|-----|----|---------|
| <b>Inputs<sup>a</sup></b>     |                                   |                 |     |     |    |         |
| Direct atmospheric deposition | 19                                | 5.6             | 24  | 5.6 | –  | 30      |
| Rivers and streams            | 177                               | 113             | 290 | 96  | 12 | 400     |
| Urban runoff <sup>b</sup>     | ~4                                | ~13             | 17  | 18  | 2  | 37      |
| Sewage treatment plants       | 6.2                               | 136             | 142 | 30  | 10 | 183     |
|                               | 206                               | 268             | 473 | 150 | 24 | 650     |
| <b>Outputs</b>                |                                   |                 |     |     |    |         |
| Export to offshore            | ?                                 | ?               | ?   | ?   | ?  | ?       |
| Denitrification               |                                   |                 |     |     |    | 85–170  |
| Hard clam harvest             |                                   |                 |     |     |    | 3.4     |
|                               |                                   |                 |     |     |    | >88–173 |
| <b>Changes in storage</b>     |                                   |                 |     |     |    |         |
| Accumulation in sediments     |                                   |                 |     |     |    | 44–97   |

<sup>a</sup> Totals may not sum because of rounding.

<sup>b</sup> DIN in runoff appeared to be approximately 25% NH<sub>4</sub> (Hanson 1982).  
Assumed organic N in runoff was partitioned as in the rivers.

Denitrification probably removes between 13 and 26% of the nitrogen entering from land and atmosphere, and some 7–17% is accumulated within the sediments of the bay. It appears that about 60–80% of the nitrogen is exported to the coastal ocean. The partitioning of that export into inorganic and organic forms will be addressed in a later section.

## *Phosphorus*

### *Inputs*

The deposition of total phosphorus from the atmosphere amounted to  $390 \mu\text{mol m}^{-2} y^{-1}$  when it was measured adjacent to the lower West Passage in 1975. (Graham 1977). This converts to a total flux onto the surface of Narragansett Bay of  $0.13 \times 10^6$  moles  $y^{-1}$ .

The flux of total phosphorus in the rivers where measurements were made amounted to  $17 \times 10^6$  moles  $y^{-1}$ . Just over 60% was in the form of DIP, 15% was DOP, and about 20% was in particulate form, though these ratios varied among the rivers (Table 17). If we follow the procedure used to calculate nitrogen input and subtract urban storm water runoff from the flow of small

*Table 17.* The annual input of phosphorus to Narragansett Bay from rivers and streams. Units are  $10^6$  moles  $y^{-1}$ .

|                               | DIP  | DOP  | PP   | Total P |
|-------------------------------|------|------|------|---------|
| Blackstone River              | 2.7  | 1.0  | 1.6  | 5.3     |
| Pawtuxet River                | 4.5  | 0.9  | 0.7  | 6.1     |
| Woonasquatucket River         | 0.16 | 0.08 | 0.12 | 0.4     |
| Moshassuck River              | 0.06 | 0.04 | 0.05 | 0.2     |
| Taunton River <sup>a</sup>    | 3.3  | 0.6  | 1.4  | 5.3     |
|                               | 10.7 | 2.6  | 3.9  | 17.3    |
| Unmeasured flows <sup>b</sup> | 2.4  | 0.6  | 0.9  | 3.9     |
|                               | 13   | 3.2  | 4.8  | 21      |

<sup>a</sup> Calculated from data of Boucher (1991) collected in 1988–1989. Other rivers measured in 1982–1983.

<sup>b</sup> Prorated on the basis of flow from the measured rivers.

streams and coastal drainage adjacent to the bay (Table 2), the latter may carry an additional  $4 \times 10^6$  moles  $y^{-1}$  into the system if their average concentrations are similar to those of the measured rivers (Table 17).

As with nitrogen, we multiplied the measured DIP storm water runoff coefficients for urban areas around the bay (Table 3) by the appropriate land use inventory (Table 4) to calculate the potential input of DIP from this source. We then used ratios of total phosphorus to DIP from the National Urban Runoff Program to estimate total P. A ratio of 4.1 was applied to the older urban areas of the Providence River and upper bay, Fall River, and Newport, and a ratio of 2.2 was applied to the newer suburban areas of East Greenwich and North Kingstown (Schueler 1987). The result suggests that storm water runoff from built up areas adjacent to the bay may add about  $2 \times 10^6$  moles of DIP  $y^{-1}$  and almost  $4 \times 10^6$  moles of total P  $y^{-1}$ .

In contrast to carbon and nitrogen, only the flux of particulate phosphorus was strongly correlated with river discharge (Fig. 7). In the Blackstone, DIP flux was relatively constant at flows above  $10 \text{ m}^3 \text{ s}^{-1}$ , while in the Pawtuxet River DIP flux showed no correlation with flow even at low discharge. Because of these results, it appears that the input of phosphorus from rivers differs little between wet and dry years. The implication of this finding is that upstream point sources provide most of the DIP and much of the DOP carried by the rivers, but that nonpoint sources are important in contributing to the load of particulate phosphorus.

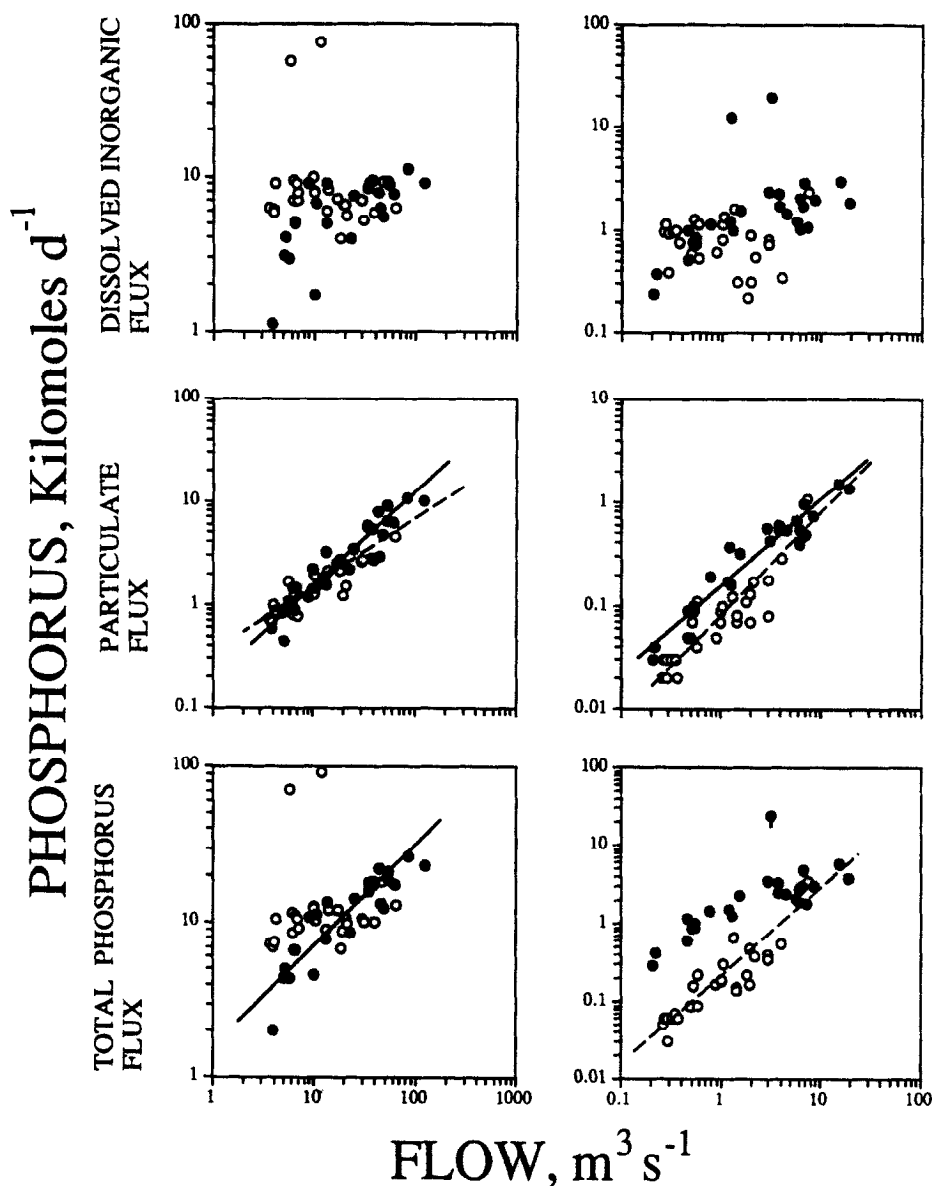


Fig. 7. Daily flux of various forms of phosphorus as a function of average daily water flow in the Blackstone (solid circles) and Pawtuxet Rivers (left) and in the Woonasquatucket (solid circles) and Moshassuck Rivers (right). Values for the intercept, slope, and  $r^2$  of the log-log regression equations for particulate phosphorus and total phosphorus were: Blackstone River (solid lines)  $-0.77, 0.92, 0.88$  and  $0.19, 0.65, 0.79$ ; Pawtuxet River  $-0.50, 0.65, 0.79$  and no significant regression; Woonasquatucket River (solid lines)  $-0.82, 0.83, 0.92$  and no significant regression; Moshassuck River  $-1.12, 0.98, 0.80$  and  $-0.73, 1.10, 0.79$ .

*Table 18.* The annual input of phosphorus to Narragansett Bay from the direct discharge of sewage treatment plants. Units are  $10^6$  moles  $y^{-1}$ .

|   | DIP  | DOP  | PP   | Total P |
|---|------|------|------|---------|
| Measured biweekly (1983)                  |      |      |      |         |
| Fields Point                              | 1.7  | 0.8  | 0.8  | 3.3     |
| Bucklin Point                             | 2.2  | 0.5  | 0.2  | 2.9     |
| East Providence                           | 0.7  | 0.06 | 0.05 | 0.8     |
|   | 4.6  | 1.4  | 1.0  | 7.0     |
| Measured 3–4 times (1985–86) <sup>a</sup> |      |      |      |         |
| East Greenwich                            |      |      |      | 0.52    |
| Quonset                                   |      |      |      | 0.09    |
| Warren                                    |      |      |      | 0.16    |
| Bristol                                   |      |      |      | 0.33    |
| Jamestown                                 |      |      |      | 0.06    |
| Newport                                   |      |      |      | 1.12    |
| Fall River                                |      |      |      | 4.53    |
|   | 4.5* | 1.4* | 0.9* | 6.8     |
|   | 9.1  | 2.8  | 1.9  | 13.8    |

\* Calculated from total P input assuming the same relative composition as the plants where measurements were obtained.

<sup>a</sup> Pilson and Hunt (1989). Monthly measurements of total P in 1992 gave values of 0.43, 0.07, 0.01, 0.25, 0.05, and 0.84, respectively, for the smaller R. I. treatment plants (Save the Bay 1992).

The remaining input of phosphorus comes from sewage treatment plants that discharge directly to the tidal waters of the bay (Fig. 1, Table 5). Taken together, these facilities release on the order of  $14 \times 10^6$  moles  $y^{-1}$  of total phosphorus. About 65% is in the form of DIP, 20% is DOP, and 15% is in particulate form (Table 18), a relative composition very similar to that of the rivers (Table 17). The much less intensive sampling program suggested total phosphorus fluxes from Fields Point, Bucklin Point, and East Providence that were factors of 2.5, 1.2, and 0.9 times our estimates, respectively. Since the Fields Point facility went through extensive repairs between the studies, and the two other results are in reasonable agreement, the 1985–1986 estimates can probably be accepted with some confidence, even though the number of samples was small. The estimates are also consistent with more recent monthly monitoring assessments (Save the Bay 1992).



### *Outputs*

The only export of phosphorus from the bay that can be quantified on the basis of some direct measurement is that removed in the clam fishery. If we assume a molar N:P ratio in clam tissue of 16, then about  $0.2 \times 10^6$  moles  $y^{-1}$  of phosphorus leave the bay along with the  $3.4 \times 10^6$  moles of nitrogen that are harvested.

### *Changes within the bay*

As discussed earlier with respect to carbon and nitrogen, the only significant accumulation of phosphorus within the bay is associated with the accretion of sediments. Unfortunately, solid phase total phosphorus analyses for sediments below the zone of bioturbation have been reported for only three areas.

Nixon and Pilson (1984) described a core from the upper bay where total P concentrations were a relatively constant  $24 \mu\text{mol g}^{-1}$  of dry sediment below the bioturbated zone. Their data from a core collected in the lower West Passage showed about  $8 \mu\text{mol P g}^{-1}$ . Beach (1981) reported  $19 \mu\text{mol P g}^{-1}$  on mid bay sediments below the mixing zone.

These values are roughly consistent with the range of  $14\text{--}31 \mu\text{mol}$  total P g dry sediment described by Howarth et al. (1995) for a variety of marine sediments analyzed by different laboratories. We assumed that sediments accumulating in the Seekonk and Providence Rivers, the Upper Bay, Greenwich Bay, Mt. Hope Bay, and the Upper East Passage (Fig. 5) contained  $25 \mu\text{mol}$  total P  $\text{g}^{-1}$ , that sediments accumulating in the Upper West Passage and the Mid East Passage contained  $20 \mu\text{mol}$  total P  $\text{g}^{-1}$ , and that sediments accumulating in the Lower West and East Passages contained  $10 \mu\text{mol}$  total P  $\text{g}^{-1}$ . By multiplying these concentrations by the mass of accumulating sediment in each region of the bay (Table 10), we calculated a total P burial of  $5\text{--}8 \times 10^6$  moles  $y^{-1}$ .

### *The annual budget*

Upstream sources appear to contribute over 50% of the total phosphorus entering the bay, and sewage treatment plants that discharge directly to the bay contribute about 35% (Table 19). Over 60% of the total phosphorus load enters as DIP, with the rest almost equally divided between DOP and particulate forms. Since only about 13–20% of the total phosphorus input appears to accumulate in the bay, there must be a large net flux through the bay to the coastal ocean. In a later section we attempt to partition that flux into dissolved and particulate organic forms using the stoichiometry of nutrient inputs to, and concentrations in, the bay.

Table 19. Current assessment of the annual mass balance of phosphorus in Narragansett Bay. See Table 17 and 18. Units are  $10^6$  moles  $y^{-1}$ .

|                               | DIP | DOP | PP  | Total |
|-------------------------------|-----|-----|-----|-------|
| <b>Inputs<sup>a</sup></b>     |     |     |     |       |
| Direct atmospheric deposition | —   | —   | —   | 0.13  |
| Rivers and streams            | 13  | 3.2 | 4.8 | 21    |
| Urban runoff <sup>b</sup>     | 2   | 0.8 | 1.2 | 4     |
| Sewage treatment plants       | 9   | 2.8 | 1.9 | 14    |
|                               | 24  | 6.8 | 7.9 | 39    |
| <b>Outputs</b>                |     |     |     |       |
| Export to Offshore            | ?   | ?   | ?   | ?     |
| Hard clam harvest             |     |     |     | 0.2   |
| <b>Changes in storage</b>     |     |     |     |       |
| Accumulation in sediments     |     |     |     | 5–8   |

<sup>a</sup> Totals may not sum because of rounding.

<sup>b</sup> The difference between total P and DIP assumed to be divided between DOP and particulates as in rivers.

### *Inputs from offshore*

In spite of the fact that there have been no direct measurements of nutrient fluxes at the mouth of Narragansett Bay, it is possible to make a rough indirect estimate of the input of C, N, and P from Block Island Sound. Pilson (1985a) analyzed an extensive set of salinity observations from the bay along with contemporaneous measurements of fresh water inflow and found that the flushing rate of the bay varied from about 10 days at high river flow to about 40 days at low flow, with an annual mean of 26 days. Officer and Kester (1991) further quantified the relationship between the input of fresh water and the inflow of offshore water due to tidal exchange and gravitational circulation that was necessary to maintain the observed salt balance.

Most of the salinity data used in the flushing calculations came from a 1972–1973 survey of various water quality parameters that included measurements of DIN and DIP (Kremer & Nixon 1978). We multiplied monthly estimates of off-shore water flow into the bay during 1972–1973 (Officer & Kester 1991) by the mean monthly concentrations of DIN and DIP measured in near-bottom water at the mouth of the East Passage during the same period (Kremer & Nixon 1978) to estimate the gross nutrient flux from offshore into the bay. The result suggests an input of about  $93 \times 10^6$  moles  $y^{-1}$  of  $NO_2 +$

$\text{NO}_3$ ,  $22 \times 10^6$  moles  $\text{y}^{-1}$  of  $\text{NH}_4$ , and  $27 \times 10^6$  moles of DIP. These values are 18% and 69%, respectively, of the total N and P inputs from land and atmosphere (Tables 16 and 19).

The coastal ocean water entering the bay also carries dissolved and particulate organic forms of C, N, and P, but the concentrations have only been measured on four occasions during 1985 and 1986 (Pilson & Hunt 1989). If those data are averaged and multiplied by the 1972–73 mean flow into the bay of  $1040 \text{ m}^3 \text{ s}^{-1}$ , the resulting fluxes come to about  $110 \times 10^6$  moles  $\text{y}^{-1}$  of PN,  $320 \times 10^6$  moles  $\text{y}^{-1}$  of DON,  $8 \times 10^6$  moles  $\text{y}^{-1}$  of PP,  $55 \times 10^6$  moles  $\text{y}^{-1}$  of DOP, and  $1800 \times 10^6$  moles  $\text{y}^{-1}$  of DOC. Since 1972–73 was a period with above average river discharge, we used the curve relating flushing rate to fresh water input developed by Officer and Kester (1991) to reduce these fluxes to those characteristic of long-term average fresh water input conditions. The resulting fluxes are about 80% of the values calculated for 1972–73. All of these must be considered very rough approximations, but it is clear that the coastal sea water entering the bay in tidal and estuarine circulation is a potentially important source of nutrients for Narragansett Bay. While it is seldom included in estuarine nutrient budgets, the importance of landward flowing bottom water in maintaining the productivity of coastal areas was pointed out over 25 years ago (Riley 1967).

### *Stoichiometry and organic export*

The ratio of total N to total P entering Narragansett Bay from the atmosphere and from land-based drainage and discharges is very similar to the Redfield Ratio and to the mean ratio of N/P found in the plankton of the bay (13:1, Nixon & Pilson 1984) (Table 20). In spite of this input and the addition of DIN and DIP from land and atmosphere in a ratio of 20:1, the mean annual volume-weighted DIN/DIP ratio maintained in the water of the bay is about 5 (Nixon & Pilson 1984). The coastal bottom water entering the bay has a DIN/DIP ratio of about 4.3, but the low ratio in the bay is not due to simple mixing. The terrestrial and atmospheric inputs are sufficiently rich in DIN that the combined DIN/DIP input from land, atmosphere, and ocean has a ratio of about 11.5. Even if the dissolved and particulate organic forms of N and P in the offshore bottom water are included, the total input N/P ratio is only reduced to 9.5. The low DIN/DIP ratio in the bay water is not a consequence of differential burial, either, because the estimated ranges of N and P accumulation in the sediments suggest that the nutrients are stored in a ratio lower than the Redfield Ratio (Tables 16 and 19).

Two processes appear to lead to and maintain the low DIN/DIP ratio of Narragansett Bay water and, hence, a condition of N limitation of primary production in the system (Oviatt et al. 1995). First, denitrification removes a

Table 20. Stoichiometry of C, N, and P inputs to Narragansett Bay.

|                           | Total C <sup>1</sup> | : | Total N | : | Total P |
|---------------------------|----------------------|---|---------|---|---------|
| Land and atmosphere total | 52–55                | : | 17      | : | 1       |
| Rivers and streams        | 86                   | : | 19      | : | 1       |
| Sewage                    | 17–24                | : | 13      | : | 1       |
| Offshore bottom water     | –                    | : | 6       | : | 1       |
| Total input               | –                    | : | 9.5     | : | 1       |
|                           | POC <sup>1</sup>     | : | PN      | : | PP      |
| Land and atmosphere total | 55–67                | : | 4       | : | 1       |
| Rivers and streams        | 78                   | : | 3       | : | 1       |
| Sewage                    | 24–74                | : | 5       | : | 1       |
| Offshore bottom water     | 225                  | : | 14      | : | 1       |
|                           | DOC                  | : | DON     | : | DOP     |
| Land and atmosphere total | 233                  | : | 20      | : | 1       |
| Rivers and streams        | 450                  | : | 30      | : | 1       |
| Sewage                    | 68                   | : | 11      | : | 1       |
| Offshore bottom water     | –                    | : | 6       | : | 1       |
|                           |                      |   | DIN     | : | DIP     |
| Land and atmosphere total |                      |   | 20      | : | 1       |
| Rivers and streams        |                      |   | 22      | : | 1       |
| Sewage                    |                      |   | 16      | : | 1       |
| Offshore bottom water     |                      |   | 4.3     | : | 1       |
| Total input               |                      |   | 11.5    | : | 1       |

<sup>1</sup> Ranges are due to uncertainties in the performance of the Fields Point sewage treatment plant. See Tables 8, 9, and 12 and text. If primary production is included, the total C:N:P ratio from land and atmosphere is 300:17:1.

significant fraction of the N entering the bay (Table 16) and, second, there is a net export of organic matter with an N/P ratio that is higher than that of the combined input of reactive N and P from all sources. Since denitrification has been quantified, it is possible to calculate the approximate amount of organic matter that must be exported or removed from the biogeochemical circulation within the bay in order to maintain the low DIN/DIP ratio that is observed.

#### *Organic export*

In our discussion of the annual carbon budget, we noted that a preliminary calculation of organic export from the bay based on the stoichiometry of nutrient inputs and nutrient concentrations in the system suggested that some

$2000 \times 10^6$  moles of organic carbon per year were lost to offshore waters (Nixon & Pilson 1984). We are now in a position to recalculate that estimate using the flux data developed in the previous sections.

The rationale for the stoichiometric calculation has been given in detail elsewhere (Nixon & Pilson 1984). Briefly, the approach treats the bay as a biochemical reactor in which N and P are added at a known rate and in a known ratio, denitrification removes N from the reactor at a known rate, organisms convert the available N and P inputs to organic matter with a known N/P ratio, organisms consume much of that organic matter thus releasing DIN and DIP, and organic matter containing N and P is removed from the reactor or accumulates in long-term storage. The exported and stored organic matter represent net "reactor" or ecosystem production that should not be confused with the much larger net production by phytoplankton and other autotrophic components of the system. The mean annual ratio of DIN/DIP observed in the "reactor" or Narragansett Bay is a result of the balance between the input ratio, denitrification, and the ratio of N/P removed from circulation in net ecosystem production. This balance can be described by a simple set of equations. In order to solve the equations for net system production, we need to specify the annual input of N and P that is available to participate in the metabolism of the bay, the N/P ratio of organic matter formed in the bay, the amount of N removed in denitrification, and the mean annual ratio of DIN/DIP in the water of the bay. Once net system production is calculated, the export to offshore can be estimated by subtracting the amount of net production sequestered in long-term storage (burial in sediments) and removed in fisheries harvest. All of these terms have been quantified in preceding tables and text except for the issue of the available N and P input.

In their sample calculation, Nixon & Pilson (1984) used only the input of DIN and DIP from land, atmosphere, and offshore. If we follow that example but use our revised input and denitrification estimates, the net total system production of Narragansett Bay is reduced to about  $970\text{--}1500 \times 10^6$  moles C  $y^{-1}$ , depending on the value of denitrification (Table 16). The removal in fisheries harvest is very small compared to other uncertainties and can be disregarded, but the accumulation of organic C in sediments may account for  $575\text{--}880 \times 10^6$  moles  $y^{-1}$  (Table 12). It thus appears that if only inorganic nutrient inputs are considered, the bay could export as little as  $90 \times 10^6$  moles C  $y^{-1}$  to offshore or perhaps as much as  $925 \times 10^6$  moles C  $y^{-1}$ . At the upper extreme, this would represent only about 10% of the estimated primary production by phytoplankton (Table 12).

It seems more realistic to assume that some of the organic N and P entering the bay also contributes to the metabolism of the system. In the absence of any direct evidence, we have assumed that all of the DON and DOP contained

in the sewage treatment plant effluents, urban runoff, and direct atmospheric deposition is labile and included in the metabolism of the bay. We have also assumed that only 25% of the DON and DOP carried by the rivers and streams is available to the organisms of the bay and that the remaining 75% is simply flushed offshore. All of the offshore organic matter is assumed to behave conservatively while it is in the bay. Finally, we have assumed that all of the particulate C, N, and P entering the bay from land is buried within the system and not metabolized. If these assumptions are later shown to be far from the truth, it will be easy to revise the calculation. In the meantime, these assumptions and revised budgets allow us to sketch tentative boundaries for the total system metabolism of Narragansett Bay and its potential exchange with offshore. Using these assumptions, the net total system production is increased to  $1250\text{--}1720 \times 10^6$  moles organic C  $y^{-1}$  or 13–18% of the primary production. If the range of burial estimates ( $575\text{--}880 \times 10^6$  moles C  $y^{-1}$ ; Table 12) is reduced by the assumed contribution of particulate C added to the bay ( $420 \times 10^6$  moles  $y^{-1}$  disregarding Fields Point treatment plant failures), it appears that  $155\text{--}460 \times 10^6$  moles  $y^{-1}$  of the total system net production is stored in bay sediments. The amount of organic matter formed in the bay and exported to Block Island Sound may thus lie between  $790\text{--}1565 \times 10^6$  moles organic C  $y^{-1}$ . This is a wide range of uncertainty, but it is none the less useful to show that the amount of autochthonous organic C leaving the bay may be less than 10% of the primary production, and that it is only about 15% even using the maximum estimate of export (Table 21).

Before leaving the discussion of total system metabolism, we should address the question of net autotrophy or heterotrophy for Narragansett Bay. The fact that the stoichiometric calculation shows that there is net ecosystem production must still be balanced against the amount of labile dissolved organic matter entering the system from land drainage and sewage. As described previously, we have assumed that 25% of the former and 100% of the latter is remineralized in the bay and that all of the particulate organic matter is refractory.

These assumptions result in the respiration of about  $550 \times 10^6$  moles of C  $y^{-1}$  ( $190 \times 10^6$  from sewage,  $360 \times 10^6$  from rivers). Since total system net production (burial plus export) lies between  $1250\text{--}1720 \times 10^6$  moles C  $y^{-1}$ , Narragansett Bay appears to be an autotrophic system with a positive carbon balance of  $700\text{--}1170 \times 10^6$  moles  $y^{-1}$  or some 7–12% of the net carbon fixation by the phytoplankton. This finding contrasts with the view of Smith (1991) and Smith and Hollibaugh (1993) that coastal systems with relatively high rates of primary production tend to be characterized by net heterotrophic system metabolism.

Table 21. The annual mass balance of C, N, and P in Narragansett Bay. Units are  $10^6$  moles  $y^{-1}$ .

|                               | C         | N         | P        |
|-------------------------------|-----------|-----------|----------|
| Inputs                        |           |           |          |
| Atmospheric Deposition        |           | 30        | 0.1      |
| Biological Fixation           | 9600      | Assumed 0 | 0        |
| Land Drainage                 | 1815      | 437       | 25       |
| Direct Sewage                 | 235       | 183       | 14       |
|                               | 11650     | 650       | 39       |
| Offshore <sup>1</sup>         |           | 115       | 27       |
|                               | 11650     | 765       | 66       |
| Outputs                       |           |           |          |
| Denitrification               |           | 85–170    | 0        |
| Clam Harvest                  | 7–14      | 3.4       | 0.2      |
| Organic Export Offshore       |           |           |          |
| Formed in the Bay             | 790–1565  | 93–185    | 7–14     |
| 75% of River DOM Input        | 1080      | 72        | 2.4      |
|                               | 1757–2634 | 240–425   | 8.6–16.6 |
| Inorganic Export <sup>2</sup> | 8100–9200 | 240–470   | 41–51    |
| Accumulation in Sediments     | 575–880   | 44–97     | 5–8      |

<sup>1</sup> DIN and DIP only. Dissolved organic and particulate inputs from offshore are very uncertain and assumed to behave conservatively while in the bay. See text.

<sup>2</sup> Calculated by difference; ranges are set by combinations of the low and high denitrification estimates (which lead to high or low estimates of autochthonous organic C, N, and P export, respectively) and upper and lower estimates of burial. Values have been rounded to two or three significant figures.

From the mean stoichiometric ratio of the organic matter formed in the bay (110:13:1, Nixon & Pilson 1984), it is possible to estimate that about  $90\text{--}185 \times 10^6$  moles  $N\ y^{-1}$  and  $7\text{--}14 \times 10^6$  moles  $P\ y^{-1}$  are also exported from the bay in organic form. With these values in hand, we can return to the annual N and P budgets (Tables 16 and 19) to estimate the net export of DIN and DIP from the bay. If we accept that the budgets must be closed, the DIN and DIP export can be calculated as the difference between previously identified total N and P inputs and the sum of denitrification, clam harvest, burial in sediments, and export in organic form. The last item is the export just calculated plus 75% of the DON and DOP added by rivers (Table 21). The overall balance suggests that Narragansett Bay retains little of the N (perhaps

5–15%) or P (perhaps 7–12%) that enters the system from all sources, and that most of the N and P is exported as DIN and DIP (Table 21).

### Comparison with experimental observations

We are fortunate in being able to compare our loosely constrained elemental budgets for Narragansett Bay with the results of more controlled mass balance studies carried out using living models or mesocosms of the bay. The mesocosms are large tanks (5 m deep, 2 m diameter, 13 m<sup>3</sup> volume) operated by the Marine Ecosystems Research Laboratory (MERL). The systems have been described often in the literature and have been operated in a variety of ways over the past 14 years to address various experimental objectives (e.g., Oviatt 1981; Donaghay & Klos 1985; Nixon et al. 1986b; Nowicki & Oviatt 1990).

Two experiments are especially relevant to the issue of C, N, and P budgets. During both of them the mesocosms were operated as well-mixed flow-through systems with a residence time of about 26 days, essentially the same as the mean for Narragansett Bay (Pilson 1985a). The tanks of interest contained a 30–40 cm thick layer of natural sediments and associated infauna from mid-bay and unfiltered water from the lower West Passage.

The first experiment was carried out in 1981–1983 and included nine tanks, three of which only received nutrients from direct atmospheric deposition and the daily water exchange with the bay. Each of the remaining six tanks received these inputs plus a daily addition of NH<sub>4</sub>, PO<sub>4</sub>, and Si (OH)<sub>4</sub> in a molar ratio of 12.8:1:0.91. The amount of nutrients added to each of the six tanks increased along a geometric series such that the most enriched tank was fertilized at a rate 32 times greater than the least enriched tank. The experiment and numerous results have been described in detail elsewhere (e.g., Frithsen et al. 1985, Oviatt et al. 1986; Nixon et al. 1986b), but the results of an input-output analysis of N and P have not been published previously. Using weekly measurements of DIN and DIP in the incoming bay water and in the outflowing mesocosm water, S. W. Nixon and A. A. Keller calculated the input and output of DIN and DIP to and from each mesocosm over a two-year period. They also estimated the input and output of PC and PN using weekly measurements of chlorophyll *a* and empirical ratios of Chl:C and Chl:N for each mesocosm (Frithsen et al. 1985; S. Jackson, personal comm.). Particulate P was calculated from PN assuming a Redfield Ratio. The results of this exercise showed that in each of the two years, virtually all of the mesocosms exported 70% or more of the DIN and DIP added, regardless of the input rate (Fig. 8). Particulate organic matter appeared to account for 15–30% of the export. This is consistent with the finding that most of the



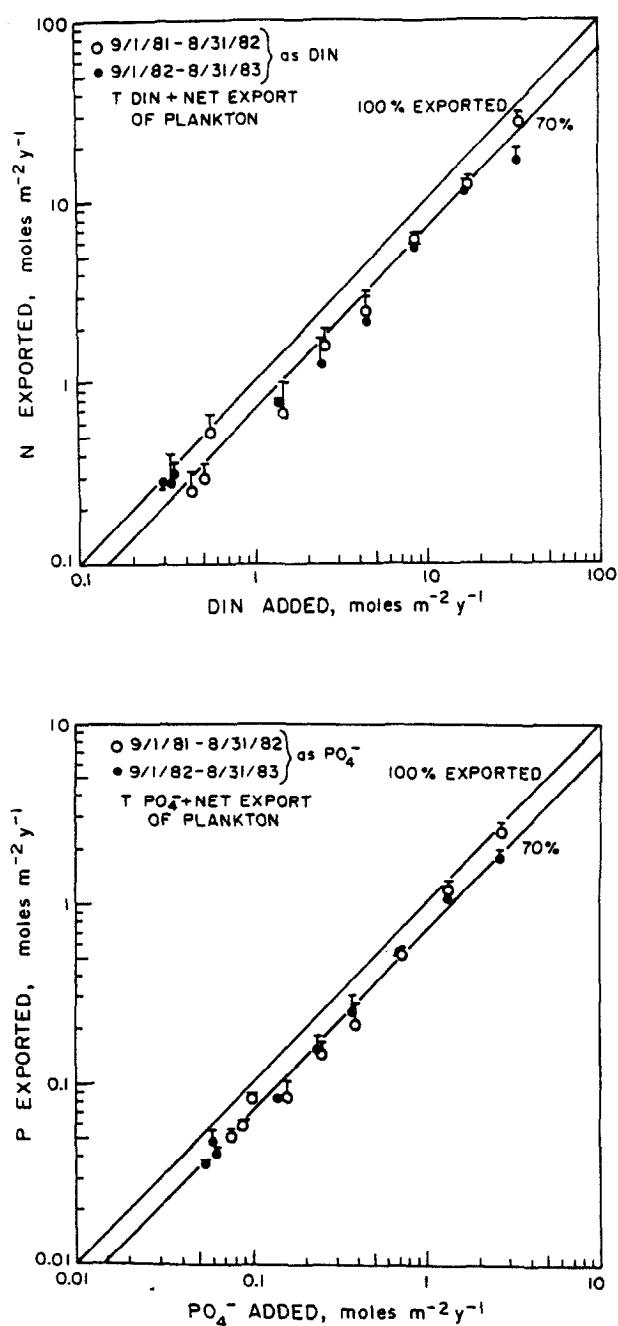


Fig. 8. The export of dissolved inorganic and particulate organic nitrogen and phosphorus from MERL mesocosms subjected to various levels of daily fertilization with DIN and DIP. During each of two years of the experiment, virtually all of the systems exported 70% or more of the nutrients added.

organic matter produced in each mesocosm, regardless of its nutrient loading rate and photosynthetic rate, was consumed within the system (Nixon et al. 1986b).

More recently, Nowicki & Oviatt (1990) described the results of even more detailed MERL mesocosm budgets that included DON and denitrification fluxes. Their study involved input-output measurements in unenriched control tanks and in tanks fertilized with  $\text{NH}_4$ ,  $\text{PO}_4$ , and Si at a rate half way along the geometric gradient used earlier. In some mesocosms, they also increased the N:Si ratio to 1. Their budgets covered two 62-day periods, one in summer and one in winter. They concluded that, "Regardless of treatment or season these experimental systems exported most of the N and P that they received. Control systems . . . retained none of the inflowing N and P during summer, and 5% of N and 25% of P inputs during winter."

The behavior of the mesocosms during both experiments was thus consistent with our more approximate calculations and estimates for Narragansett Bay as a whole (Table 21).

### Some conclusions and implications

We began this assessment of the mass balance of C, N, and P in Narragansett Bay by recognizing James Johnstone's (1908) pioneering efforts to develop a nitrogen budget for the North Sea. At the end of our effort it is humbling to admit that the caution he expressed almost a century ago is still appropriate for our much smaller system — "It is not possible to set, in balance-sheet fashion, these receipts and outputs against each other. We know only very imperfectly what are the approximate masses of nitrogen compounds in circulation." Some aspects of the biogeochemical behavior of Narragansett Bay have, however, become clearer.

The largest part by far of each of these biologically important elements enters Narragansett Bay in inorganic form. Even in this system with an urban shoreline and a densely developed watershed (about 390 persons  $\text{km}^{-2}$  in 1985), organic carbon fluxes from land amounted to only some 20% of primary production. An unknown fraction of the primary production, however, is supported by anthropogenic nutrient enrichment. There is no question that the metabolism of Narragansett Bay has been altered greatly by human actions. Biological fixation of inorganic carbon in the bay is sufficiently large that it can not be sustained by the inputs of N and P alone, even if the organic forms of N and P are considered. Primary production probably requires on the order of  $1500 \times 10^6$  moles of N and  $90 \times 10^6$  moles of P each year, or about 2 and 1.5 times the total input, respectively. Since much of the N and P from land drainage is added to the bay during winter, when there is little

biological demand, the importance of nutrient regeneration in maintaining the productivity of the system is evident.

The amount of nitrogen entering Narragansett Bay from upstream land drainage and sewage is about 2.5 times greater than the amount from direct sewage discharges. Most (72%) of the nitrogen in the river is in the form of DIN, but  $\text{NH}_4$  accounted for almost 40% of the DIN. The all too common practice of describing riverine N loads in terms of  $\text{NO}_2$  and  $\text{NO}_3$  alone is inappropriate, at least for urban watersheds. DON comprised about 25% of the river N load and it should be a high priority to determine the fate of this material. Direct deposition of N from the atmosphere (including all forms of N) provided only about 4% of the total N input, but the relative contribution of atmospheric deposition, sewage, and fertilizer to the N burden of the rivers is not known. The amount of N entering the bay from land drainage appears to vary by a factor of two between dry and wet years, thus indicating the importance of non-point sources of this nutrient. Landward flowing bottom water from offshore may provide a flux of DIN equal to 15–20% of the total N input from other sources. At certain times of year, however, when DIN is depleted in the water within the bay, this input from offshore may make an important contribution to the productivity of the system. The possibility deserves further study.

The flux of DIP from offshore into Narragansett Bay appears to be approximately the same as the flux from land drainage and upstream sewage and fertilizer. Direct sewage discharges to the bay provide about 20% of the total P input. DIP inputs from land-based sources are about three times greater than DOP inputs, and the DOP flux is essentially equal to the flux of particulate phosphorus. The input of DIP varies little between wet and dry years, reflecting the importance of point sources for this nutrient.

Sediment deposition rates over most of Narragansett Bay appear to be low, and only a small fraction (perhaps 5–10%) of the organic matter formed in the bay is buried. Because the bay is shallow, a significant amount (perhaps 25%, Nixon et al. 1976, 1986b) of the fixed organic matter is decomposed in anoxic bottom sediments, thus allowing denitrifying bacteria to remove 10–25% of the total N input to the system. Another portion of the organic matter (perhaps 10–20%) is exported to coastal waters offshore.

The greatest share of the organic matter formed in the bay (perhaps 75–85%) is consumed within the system and primarily within the water column. Because of this, almost all of the N and P that enters the bay in inorganic form is finally exported in inorganic form to the waters offshore. On average, the anthropogenically generated nutrients that enter Narragansett Bay from land and atmosphere do not remain for long and there is little record of their

passing. During the time they are in the bay, however, their impact on the biology of the system may be profound.

Mass balances for C, N, and P have been developed recently for several other coastal marine ecosystems, and it is interesting and useful to compare them with our assessment for Narragansett Bay. The results of a collaborative effort along these lines will appear in a forthcoming special issue of *Biogeochemistry* (Nixon et al. in press).

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### Note

\* We are pleased to dedicate this paper to Norbert Jaworski on the occasion of his retirement as Director of the U. S. E.P.A. Marine Environmental Research Laboratory, Narragansett, RI. Throughout his career Norb has had a great appreciation for the mass balance as an important research and management tool.

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