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## Some challenges of an “upside down” nitrogen budget – Science and management in Greenwich Bay, RI (USA)

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### ABSTRACT

When nutrients impact estuarine water quality, scientists and managers instinctively focus on quantifying and controlling land-based sources. However, in Greenwich Bay, RI, the estuary opens onto a larger and more intensively fertilized coastal water body (Narragansett Bay). Previous inventories of nitrogen (N) inputs to Greenwich Bay found that N inputs from Narragansett Bay exceeded those from the local watershed, suggesting that recent efforts to reduce local watershed N loads may have little effect on estuarine water quality. We used stable isotopes of N to characterize watershed and Narragansett Bay N sources as well as the composition of primary producers and consumers throughout Greenwich Bay. Results were consistent with previous assessments of the importance of N inputs to Greenwich Bay from Narragansett Bay. As multiple N sources contribute to estuarine water quality, effective management requires attention to individual sources commensurate with overall magnitude, regardless of the political complications that may entail.

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### 1. Introduction

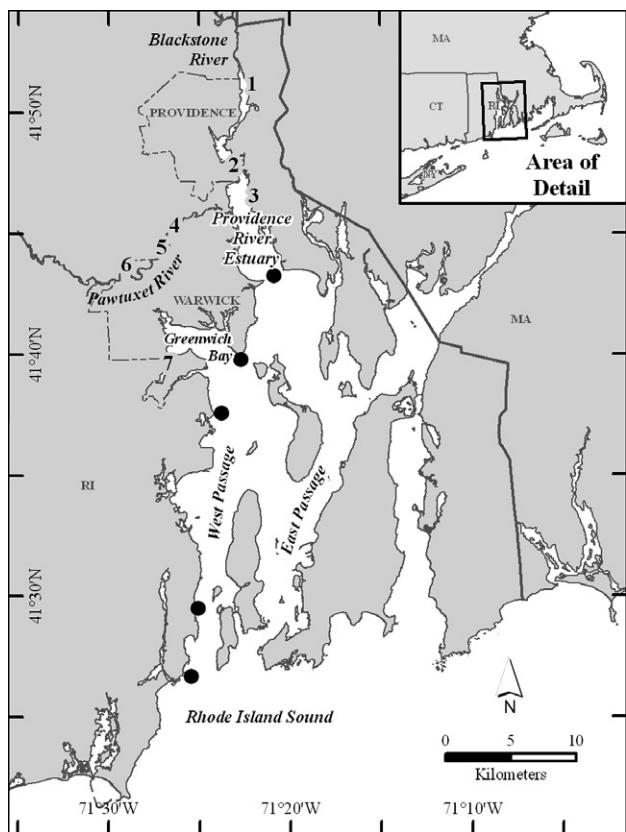
Greenwich Bay is a small ( $12 \text{ km}^2$ ), shallow (mean depth of 2.6 m) embayment in the northwest corner of Narragansett Bay, RI (Fig. 1) that is locally famous for its dense populations of hard and soft shell clams (*Mercenaria mercenaria* and *Mya arenaria*, respectively). The recent history of Greenwich Bay is familiar and repeated all along the New England coast, where after the Second World War a few houses became many, summer cottages became year round homes, and population density began to increase rapidly (now 875 people  $\text{km}^{-2}$ ; [Greenwich Bay Special Area Management Plan, 2005](#)). Sewage disposal became a complex mix of dysfunctional cesspools, septic tanks, and leach fields of varying age and effectiveness. Warwick, the largest city on Greenwich Bay, constructed a small sewer system and treatment plant that discharged to the nearby Pawtuxet River in 1965, but few of the city's population of about 69,000 were connected ([Warwick Sewer Authority \(WSA\), 2006](#)). By 1992, bacterial contamination caused the state Department of Environmental Management (RIDEM) to close the bay to shell fishing.

This dramatic management action highlighted the waste water problem and generated strong community support for cleaning up the bay ([Kennedy and Lee, 2003](#)). The resultant “Greenwich Bay Initiative” was led by the city of Warwick and consisted of many projects supported by local, state, and federal agencies whose goal was to locate critical habitats, identify pollution sources and impacts, and recommend and implement corrective actions. One part of the initiative ([Granger et al., 2000](#)) involved documenting sources and impacts of nitrogen (N), the nutrient whose supply most strongly limits primary production in this system ([Kremer and Nixon, 1978; Oviatt et al., 1995](#)). Accounting for nutrient inputs is a first step in developing budgets or mass balances as a guide for nutrient management and a check on estimates of ecosystem metabolism and biogeochemical cycling ([Boynton and Nixon, in press](#)). While N and phosphorus (P) budgets had been developed for Narragansett Bay as a whole ([Nixon et al., 1995](#)), such information had never been assembled for Greenwich Bay itself.

The total annual N input to Greenwich Bay was estimated by [Granger et al. \(2000\)](#) to be  $9.6\text{--}16.6 \times 10^6$  moles. The major uncertainty contributing to this range was in the flux of dissolved inorganic N (DIN) into Greenwich Bay from the upper West Passage of Narragansett Bay proper due to tidal advection and gravitational circulation (Fig. 1). Rough box model calculations combined with DIN concentration measurements suggested an annual input of  $3.6\text{--}9.4 \times 10^6$  moles from Narragansett Bay compared with

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**Fig. 1.** Narragansett Bay and the Providence River Estuary, RI. The Blackstone River is the largest river entering the Providence River estuary just north of Providence while the second largest source of fresh water to the estuary, the Pawtuxet River, enters just south of Providence. The major RI sewage treatment plants are numbered with the population (thousands) connected in 2003 shown in () based on data from RIDEM: 1 = Bucklin Pt (120); 2 = Fields Pt. (209); 3 = East Providence (48); 4 = Warwick (28); 5 = Cranston (77); 6 = West Warwick (30); 7 = East Greenwich (2.5). Numerous additional plants discharge to the Blackstone River. Solid circles are locations of Narragansett Bay water sampling for DIN concentrations and stable isotope values.

$5\text{--}7.3 \times 10^6$  moles from the watershed (including streams, groundwater, and a small sewage treatment plant serving the town of East Greenwich), and  $1.1 \times 10^6$  moles  $\text{y}^{-1}$  from direct atmospheric deposition. The annual inputs calculated by Granger et al. (2000) stimulated Brush (2002) to develop a more detailed analysis of daily N inputs over an annual cycle. His results suggested that the total N input from upper Narragansett Bay (DIN plus phytoplankton particulate N) was even larger relative to the watershed DIN sources ( $16.9 \times 10^6$  vs.  $3.8 \times 10^6$  moles), though there was a marked seasonality with watershed sources dominating during spring and early summer. We characterize the N budget for Greenwich Bay as “upside down” because the largest input to the system comes from the mouth or salt water source for the estuary rather than the head or fresh water source (Boynton and Nixon, in press). Considering that Narragansett Bay proper is heavily fertilized by rivers and sewage treatment plants that discharge to the Providence River estuary “upstream” of Greenwich Bay (Nixon et al., 2008), it did not seem improbable to Granger et al. (2000) or Brush (2002) that N from the Providence River estuary could be the largest source of N to Greenwich Bay (Fig. 1).

These results were published with little notice until a large fish kill took place in Greenwich Bay during August of 2003 (RIDEM, 2003). The fish kill was clearly linked to anoxic conditions that were attributed to N enrichment from local watershed sources, especially cesspools and septic systems, the small East Greenwich sewage treatment plant, and lawn fertilizer (WSA, 2006). Just as

the closure of the bay to shell fishing eleven years earlier had focused attention on bacterial pollution, the fish kill now focused attention on N sources to the bay. Again, the City of Warwick with the greatest concentration of population in the watershed (about 86,000 people in 2000) took a lead and increased efforts to get households to abandon their on-site sewage disposal and connect their houses to an expanding city sewage system that was now linked to an upgraded sewage treatment plant on the Pawtuxet River (Fig. 1), thus lowering the N loading to Greenwich Bay from septic systems. While the city has had a mandatory sewer connection program since 1992, households around Greenwich Bay have been slow to comply (WSA, 2006).

As political pressure on homeowners to connect with the sewer system increased, some took notice of the Granger et al. (2000) and Brush (2002) inventories of N inputs and objected that while septic systems might be providing some 50% of the watershed input to the Greenwich Bay, the watershed input was only equal to or possibly smaller than the input from Narragansett Bay. They argued that the far field sources of N being discharged to the Providence River estuary by the Blackstone River, the City of Providence, and, in fact, the Pawtuxet River and its three sewage treatment plants (including that from the City of Warwick) were as important, if not more, in stimulating algal blooms in Greenwich Bay than were local septic systems. The “upside-down” N budget thus became a subject for vigorous debate between managers and the research community.

The stable isotope measurements we report here were made in an effort to resolve the issue of how important the input of N from Narragansett Bay proper might be in the ecology of Greenwich Bay. We measured stable isotopes ( $\delta^{15}\text{N}$ ) of the major N sources from the local watershed and from Narragansett Bay to compare with the  $^{15}\text{N}$  in organisms from the inner and outer portions of the coves and open waters of Greenwich Bay over an annual cycle. We also once again evaluate the magnitude of the sources of N to Greenwich Bay during the period when water and organisms were being collected so that the isotope results could be combined with N flux data in a mass balance calculation to aid in interpretation.

While we recognize that not all N sources are isotopically distinct, characteristic values do exist for several sources of particular interest in Greenwich Bay. Secondary treated wastewater effluent and septic leachate to groundwater generally have  $\delta^{15}\text{N}$  values between 7‰ and 30‰ (McClelland and Valiela, 1998a; Sheats, 2000; Tucker et al., 1999) while offshore dissolved inorganic nitrogen (DIN) typically ranges between 1‰ and 7‰ (Chaves, 2004; Holmes et al., 1998). Nitrate ( $\text{NO}_3^-$ ) and ammonium ( $\text{NH}_4^+$ ) in atmospheric deposition tend to range between  $-10\text{‰}$  and  $8\text{‰}$  (Heaton, 1986; Macko and Ostrom, 1994; Mayer et al., 2002). Fertilizer  $\text{NO}_3^-$ , because it is synthesized with atmospheric N ( $\delta^{15}\text{N} = 0\text{‰}$ ), is between  $-3\text{‰}$  and  $3\text{‰}$  (Mayer et al., 2002; McClelland and Valiela, 1998a; McKinney et al., 2001). However, source separation by nitrogen isotope value alone is confounded not only by overlapping ranges, but by transformations that N species can undergo during transit from source to biological uptake. While  $\delta^{15}\text{N}$  values typically fractionate during uptake, with the heavier isotope increasing in abundance at each trophic step, this fractionation is often species and tissue specific (e.g. Caut et al., 2009; Oczkowski et al., 2008). Yet, while food web components may reflect their source N differently, they are taking up an integrated DIN signature and cannot discriminate among different N sources.

## 2. Methods

### 2.1. Study site

Greenwich Bay is a phytoplankton based system with primary production based on  $^{14}\text{C}$  uptake estimated at  $220\text{--}250\text{ g C m}^{-2}\text{ y}^{-1}$

(Oviatt et al., 2002). The watershed of the bay is approximately 54.8 km<sup>2</sup> of which some 65% is developed (Granger et al., 2000). Semidiurnal tides have a mean range of 1.1 m and the mean water residence time for the bay as a whole is about 8.8 days (Brush, 2002). The coves are characterized by shorter residence times of between 0.3 (Brushneck) and 4.2 (Warwick) days (Brush, 2002; Erikson, 1998; Granger et al., 2000; Spaulding et al., 1998). Direct freshwater inputs average 1.3 m<sup>3</sup>sec<sup>-1</sup>, which includes the East Greenwich Wastewater Treatment Facility (WWTF) located in Greenwich Cove (Fig. 2). The largest three streams that drain the Greenwich Bay watershed, the Hardig, Maskerchugg, and Tuskatucket, discharge at the upper portions of Apponaug, Greenwich, and Brushneck Coves, respectively, and receive no direct effluent discharge (Fig. 2). Daily flow volumes have been estimated at 16,500, 16,100, and 5400 m<sup>3</sup>, respectively, representing over 90% of stream contributions to Greenwich Bay (Urish and Gomez, 2004). Salinity throughout Greenwich Bay varies between about 25 and 30 and water temperatures range from near 0 to 30 °C over an annual cycle. The inner and mid regions of the bay experience intermittent hypoxic conditions during summer (Brush, 2002; Granger et al., 2000).

## 2.2. Water collection

Estuarine water samples were collected from Greenwich Bay and Narragansett Bay six times between August 2004 and November 2005 (Figs. 1 and 2). Near-surface and near-bottom samples were collected in Narragansett Bay, while only surface samples were collected in Greenwich Bay and its coves.

Surface water samples were collected from each of the three streams on six occasions between July 2004 and July 2005 (Fig. 2). Stream samples were collected after a 3 day period with no precipitation.

Groundwater samples were collected from surface seeps at four sites along the shoreline of Greenwich Bay located from thermal infrared aerial imagery taken in the summer of 1997 (Aero-Marine Surveys, Inc. August 24, 1997). The seeps were sampled five times between October 2004 and November 2005 (Fig. 2). Groundwater was collected, where possible, from surficial water pooling in a shallow excavation or, more frequently, from installed piezometers during the 1.5 h preceding ebb tide through approximately the first hour of flood after verifying low salinity (<5.0 psu) with a hand-held refractometer.

While 105 storm water outfalls have been identified within the Greenwich Bay watershed, we sampled two of those measured to have the highest concentrations and loads of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> (Wright et al., 1998). Although we only sampled two storm water outfalls, by selecting the two sites with the highest known concentrations, we likely overestimate, rather than underestimate, their influence. Each site was sampled during three rain events of sufficient precipitation to generate moderate discharge between November 2004 and July 2005. Samples were collected during the initial 2–3 h of rainfall following at least a 3 day dry period. No ice or snow was present on the ground during cold weather sampling.

The East Greenwich WWTF (Fig. 2) was sampled eight times between August 2004 and June 2005. Discharge during the period of this study averaged 5224 m<sup>3</sup>d<sup>-1</sup>, consistent with the long-term average of 4542 m<sup>3</sup>d<sup>-1</sup> (January '01–December '05, East Greenwich WWTF Daily Maintenance Records, U.S. EPA PCS, 2006). During our

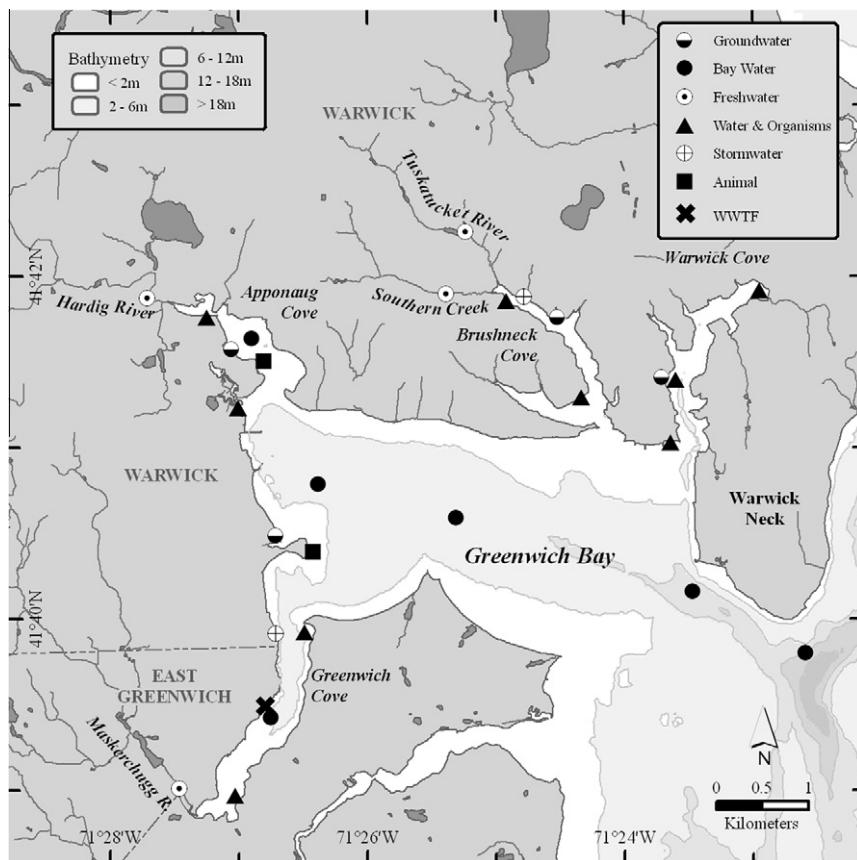


Fig. 2. Detailed map of Greenwich Bay showing sampling locations for nutrient concentrations and stable isotopes in watershed DIN sources and bay waters. Sampling stations for organisms analyzed for <sup>15</sup>N are also shown.

investigation, sewage underwent primary and secondary treatment and was disinfected with UV light. Samples were drawn from routine weekly 24 h composite collections.

Water samples for  $\delta^{15}\text{N}$  analysis were filtered through pre-combusted Whatman GF/F microfibre filters and stored in acid washed amber HDPE containers. Salinity was recorded with a YSI 30 SCT probe and samples were preserved by adjusting the pH to 2.0 with concentrated sulfuric acid. Prior to acidification, an aliquot of filtered water was removed and placed in an acid washed 60 ml HDPE vial and frozen for later nutrient analysis ( $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and  $\text{NH}_4^+$ ) by means of a Latchat Model 8000 flow injection auto analyzer according to standard methods (Grasshoff, 1983).

### 2.3. Water analysis for $\delta^{15}\text{N}$ of $\text{NO}_3^-$ and $\text{NH}_4^+$

Both fresh and estuarine water samples were analyzed for  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$  plus  $\text{NO}_2^-$  following the method of McIlvin and Altabet (2005) and for  $\text{NH}_4^+$  following the method described in Zhang et al. (2007). The  $\delta^{15}\text{N}$  values were measured simultaneously and standard deviations were generally less than 0.2‰. Analyses were performed at the School of Marine Science and Technology (SMAST) at the University of Massachusetts, Dartmouth.

Of the 166 estuarine/fresh water samples collected, only 64 met both minimum analytical concentration and detection requirements, where enough nitrogen was measured on the mass spectrometer to yield a reproducible  $\delta^{15}\text{N}$  value (DiMilla, 2006). Complete analysis of the 61 samples run for  $\delta^{15}\text{N}$  in  $\text{NO}_3^-$  and  $\text{NH}_4^+$  resulted in 54 individual measurements of nitrate  $\delta^{15}\text{N}$  and 19 for ammonium  $\delta^{15}\text{N}$ .

### 2.4. Organism collections

We sampled common primary producers (macroalgae) and consumers from the upper and lower portions of the four largest coves and along the perimeter of the shoreline five times between July 2004 and July 2005 (Fig. 2; DiMilla, 2006). Target organisms included two species of macroalgae: *Ulva lactuca* and *Gracilaria* spp., three species of bivalves: *Geukensia demissa*, *Mya arenaria*, and *Mercenaria mercenaria*, and the mummichog, *Fundulus heteroclitus*. On a few occasions (July, August 2004 and June, July 2005), silversides (*Menidia menidia*) and juvenile winter flounder (*Pseudopleuronectes americanus*) were collected from Apponaug Cove and the western shoreline of Greenwich Bay. Consumer samples consisted of at least five specimens of the smallest individuals available to provide the most recently incorporated isotope value possible. Winter flounder were an exception as they were analyzed individually after removing the gut, head, and caudal fin. Additional collections of *Mercenaria* were sampled from both Greenwich Bay proper and Narragansett Bay during the Rhode Island Department of Environmental Management (RI DEM) annual survey in summer 2005 (DiMilla, 2006). The DEM collected subtidal *Mercenaria* across the main stem of Greenwich Bay via hydraulic dredge. All samples were dried at 60 °C for at least 2 days and ground with a mortar and pestle to a fine powder. *Geukensia* was prepared whole, but isolated tissues were taken from *Mya* (siphon) and *Mercenaria* (foot); fish were gutted and dried whole.

The  $\delta^{15}\text{N}$  values were determined using a continuous flow isotope ratio mass spectrometer (CF-IRMS) at the US Environmental Protection Agency, Atlantic Ecology Division in Narragansett, Rhode Island. Samples were run in duplicate on a Carlo-Erba NA 1500 Series II Elemental Analyzer connected to a Micromass Optima Mass Spectrometer with a precision of  $\pm 0.3\text{\textperthousand}$  (McKinney et al., 2001). Isotope ratios were calculated as:

$$\delta^{15}\text{N} = [(R_{\text{sample}}/R_{\text{standard}} - 1)] \times 10^3$$

where  $R$  is the ratio of the heavy to light isotope ( $^{15}\text{N}/^{14}\text{N}$ ). Raw values were corrected to a working standard (dogfish muscle, DORM-1, National Research Council Canada;  $\delta^{15}\text{N} = 11.2 \pm 0.06\text{\textperthousand}$ ) run in triplicate on each run and expressed as a parts per thousand (parts per mil) deviation from the standard.

### 2.5. Statistical analysis

Statistical evaluation of  $\delta^{15}\text{N}$  values was accomplished through one-way ANOVA (Zar, 1999) grouped by various parameters using SPSS 11.0 statistical software. To assess seasonal variability, collections were placed into one of five "collection brackets" that corresponded most closely to actual collection date (i.e. July 2004, October 2004, February 2005, April 2005, and July 2005). Normality of the data was assessed using a Shapiro-Wilkes test. A Levene test was performed to determine homogeneity of variance. If a significant result was obtained, a Kruskal-Wallis test (Zar, 1999), a nonparametric ranked ANOVA, was also performed to verify the one-way ANOVA result. Post hoc analysis to determine related comparisons was performed using a Bonferroni test. If the Levene statistic indicated heterogeneous variance, a Tamhane post hoc test was also performed to compare to the Bonferroni result. The Tamhane post hoc analysis does not assume equal variance (Rafter et al., 2002).

## 3. Results

### 3.1. Nitrogen isotope ratios of sources

With the exceptions of groundwater and storm drain runoff, average ammonium  $\delta^{15}\text{N}$  values were considerably enriched compared with nitrate  $\delta^{15}\text{N}$  values from the same source (Table 1).  $\text{NH}_4^+$  values averaged 14.23‰ in Greenwich Bay and 12.06‰ in the surface waters of Narragansett Bay. Nitrate in Greenwich Bay water appeared to be enriched (4.41‰) compared with  $\text{NO}_3^-$  in Narragansett Bay (2.28‰, Table 1). With the exception of a July 2005 collection from Tuskatucket stream (13.74‰), the heaviest ammonium  $\delta^{15}\text{N}$  values were found in Greenwich Bay and upper Narragansett Bay.

Average  $\delta^{15}\text{N}$  values of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in groundwater were low, 4.62‰ and 2.00‰, respectively (Table 1). The average stream nitrate  $\delta^{15}\text{N}$  value (6.93‰) is similar to those measured in the nearby Blackstone River (Fig. 1; Chaves, 2004; Mayer et al., 2002). Seasonal variability noted in other systems (Cifuentes et al., 1989) was not seen in our study, and there was no significant difference in N isotope values among individual streams.

Ammonium  $\delta^{15}\text{N}$  values in the effluent from the small sewage treatment plant averaged 11.24‰ (Table 1) while  $^{15}\text{NO}_3^-$  values

**Table 1**

Summary of  $\delta^{15}\text{N}$  in DIN sources to Greenwich Bay, RI including freshwater, direct sewage discharge (WWTF), estuarine, and near shore Block Island Sound. Analyses of Greenwich Bay water are also included. Concentrations are averages of all samples collected.

Sources	$\delta^{15}\text{N-NO}_3^-$				$\delta^{15}\text{N-NH}_4^+$			
	%	S.E.	n	Conc. ( $\mu\text{M}$ )	%	S.E.	n	Conc. ( $\mu\text{M}$ )
Storm drains	7.84	0.82	5	279	2.74	0.15	2	48
Streams	6.93	0.29	16	169	12.24	1.50	2	9.2
Groundwater	4.62	0.77	9	279	2.00	0.21	2	12
WWTF	6.84	0.78	7	422	11.24	0.46	5	288
Greenwich Bay	4.41	0.77	11	7.4	14.23	0.51	3	2.8
Narragansett Bay	2.28	1.13	6	2.6	10.74	0.96	5	2.3
Surface	2.54	1.30	4	2.5	12.06	0.80	3	2.2
Bottom	1.76	2.97	2	2.2	8.75	0.76	2	2.3

**Table 2**

Estimated annual DIN contributions to Greenwich Bay from individual sources based upon annual flow volumes and measured concentrations. See text for details and sources of data.

Source	Flow $10^6 \text{ m}^3 \text{ yr}^{-1}$	$\text{NO}_3^-$ μM	$\text{NH}_4^+$ μM	$\text{NO}_3^-$ $10^3 \text{ moles yr}^{-1}$	$\text{NH}_4^+$ $10^3 \text{ moles yr}^{-1}$	DIN $10^3 \text{ moles yr}^{-1}$	%
Narragansett Bay Streams	1250 25	3.3 169	5.7 9.2	4.1 4.2	7.1 0.2	11.2 4.4	54 21
Groundwater	8.3	279	12.4	2.3	0.1	2.4	12
E.G. WWTF	1.9	422	288	0.8	0.6	1.4	7
Storm drains	2.6	279	48.3	0.7	0.1	0.9	4
Wet deposition	16	16.9	9.6	0.3	0.2	0.4	2
		Total		12.4	8.3	20.7	100

were lower (mean = 6.84‰) and fluctuated more widely, from 3.92‰ to 9.45‰. Values are consistent with those measured in Delaware Bay treatment plants, where  $\delta^{15}\text{NH}_4^+$  ranged from 8.8‰ to 18.2‰ and  $\delta^{15}\text{NO}_3^-$  ranged from -5‰ to 10.7‰ (Sheats, 2000). Storm drain water had the highest average  $\delta^{15}\text{NO}_3^-$  of any source, 7.84‰, but a low  $\delta^{15}\text{NH}_4^+$  of 2.74‰. The average  $\text{NO}_3^-$  concentration (279 μM) was high and identical to that of groundwater (Table 1). The average  $\text{NH}_4^+$  concentration in stormwater was also high relative to the other sources (48 μM).

### 3.2. Nitrogen inputs

Measured DIN concentrations and water input estimates were used to calculate N input fluxes during the study period. Annual discharge from the East Greenwich WWTF over the period of our investigation was  $1.9 \times 10^6 \text{ m}^3 \text{ yr}^{-1}$ , according to facility records. Direct wet deposition was estimated to be  $16 \times 10^6 \text{ m}^3 \text{ yr}^{-1}$  using annual rainfall of 131 cm measured by NOAA at nearby T.F. Green airport in Warwick and a surface area of Greenwich Bay of 12.0 km<sup>2</sup>. Our isotope studies were thus carried out during a relatively wet year compared with the long-term (1905–2006) mean wet deposition of 108 cm  $\text{yr}^{-1}$  (Pilson, 2008). Total freshwater input during the study was approximately  $1.7 \text{ m}^3 \text{ s}^{-1}$ . Values for rain DIN concentration were obtained from the closest National Atmospheric Deposition Program National Trends Network (NADP/ NTN) site in Connecticut (Lehmann et al., 2005; National Atmospheric Deposition Program (NRSP-3), 2011). Storm drain discharge was estimated at  $2.6 \times 10^6 \text{ m}^3 \text{ yr}^{-1}$  by averaging the results of two methods. The first extrapolated from measured flow volumes during a sampling of 17 storm drains in the Greenwich Bay watershed ( $3.3 \times 10^6 \text{ m}^3 \text{ yr}^{-1}$ ; Wright et al., 1998); the second estimated storm drain flow by coupling the rise in stream flow with the amount of rainfall during a known period and applying this ratio to the amount of impervious surface in the watershed ( $2.1 \times 10^6 \text{ m}^3 \text{ yr}^{-1}$ ; DeMelo, 1996; DiMilla, 2006; Wright and Viatore, 1999; L. Joubert, personal communication). Combined groundwater and streamflow were taken from Brush (2002) and total freshwater inflow was allocated to stream flow (75%) and groundwater (25%) following Gomez (1998). Calculated values for streams and groundwater were  $25.0 \times 10^6$  and  $8.33 \times 10^6 \text{ m}^3 \text{ yr}^{-1}$ , respectively. Annual flow of Narragansett Bay water into Greenwich Bay calculated by Brush, (2002;  $1.25 \times 10^9 \text{ m}^3 \text{ yr}^{-1}$ ) was coupled with DIN concentrations for the upper West Passage of Narragansett Bay from Granger et al. (2000), as Granger et al. (2000) sampled nutrients 19 times (5/1996–5/1997) compared to our six seasonal collections. Mean concentrations were 3.32 μM for  $\text{NO}_3^-$  plus  $\text{NO}_2^-$  and 5.68 μM for  $\text{NH}_4^+$ .

We estimate that Greenwich Bay received approximately  $11.2 \times 10^3$  moles of DIN during the year of our study ( $157 \text{ kg N yr}^{-1}$ ; Table 2). The largest source was Narragansett Bay, contributing about 54% of the annual total. Stream contributions amounted to 21%, while groundwater represented 12%. The

input from the WWTF (7%) was equivalent to that of storm drain discharge and wet deposition on the surface of Greenwich Bay combined (Table 2).

### 3.3. Organisms

There was no statistically significant seasonal variability in the  $\delta^{15}\text{N}$  of any of the organisms with the exception of *Ulva* between the April 2005 and July 2005 collections and *Mercenaria* between the October 2004 and July 2005 collections. Further, there were no significant differences in  $\delta^{15}\text{N}$  between the upper and lower portions of the coves for any species, with the exception of *Mya*, where there was an almost fivefold difference in sample size between the upper and lower coves (upper  $n = 4$ ; lower  $n = 19$ ; Table 3). Only two organisms, *Geukensia* and *Fundulus*, exhibited significant spatial differences among the coves – in both cases only between Brushneck and Greenwich Coves. *Geukensia* from Brushneck Cove were 0.63‰ heavier than Greenwich Cove and *Fundulus* were 1.04‰ heavier. DIN concentrations in both Apponaug and Greenwich coves were periodically high (>40 M during the spring and early summer; Brush, 2002). There were no significant spatial differences in the *Mercenaria* collected by the RI DEM within the open waters of Greenwich Bay or between the open bay and the coves (Table 3). *Pseudopleuronectes* collected in August 2004 from Apponaug Cove ( $n = 3$ ) and July 2005 from western Greenwich Bay ( $n = 5$ )

**Table 3**

One-way ANOVA analysis results between upper and lower cove sites and mainstem using mean  $\delta^{15}\text{N}$  values for primary producers and consumers in Greenwich Bay. S.E. is standard error and N is the number of individuals measured. Due to small sample size and weak spatial distribution, winter flounder (*Pseudopleuronectes americanus*) and silversides (*Menidia menidia*) were not included in these analyses.

	$\delta^{15}\text{N}$	S.E.	N	P-value
<i>Macroalgae</i>				
Green algae ( <i>Ulva</i> sp.)				
Upper coves	10.93	0.42	15	0.825
Lower coves	10.80	0.37	16	
Red algae ( <i>Gracilaria</i> sp.)				
Upper coves	10.72	0.80	4	0.213
Lower coves	11.51	0.25	13	
<i>Consumers</i>				
Hard clam ( <i>Mercenaria mercenaria</i> )				
Upper coves	12.53	0.12	14	0.137
Lower coves	12.78	0.11	14	
Mainstem	12.65	0.05	43	
Ribbed Mussel ( <i>Geukensia demissa</i> )				
Upper coves	10.55	0.16	15	0.912
Lower coves	10.52	0.11	17	
Soft-shell clam ( <i>Mya arenaria</i> )				
Upper coves	10.78	0.28	4	0.044*
Lower coves	11.37	0.11	19	
Mummichog ( <i>Fundulus heteroclitus</i> )				
Upper coves	13.94	0.24	12	0.383
Lower coves	14.19	0.13	10	

\* Values are significantly different.

had mean  $\delta^{15}\text{N}$  values of 13.8‰ and 14.2‰, respectively. The  $\delta^{15}\text{N}$  values for silversides (*Menidia menidia*) were similarly high, with mean values ranging from 13.8‰ to 14.2‰ in lower Apponaug Cove and western Greenwich Bay during four samplings ( $n \geq 9$  per station and date) in the summers of 2004 and 2005.

#### 4. Discussion

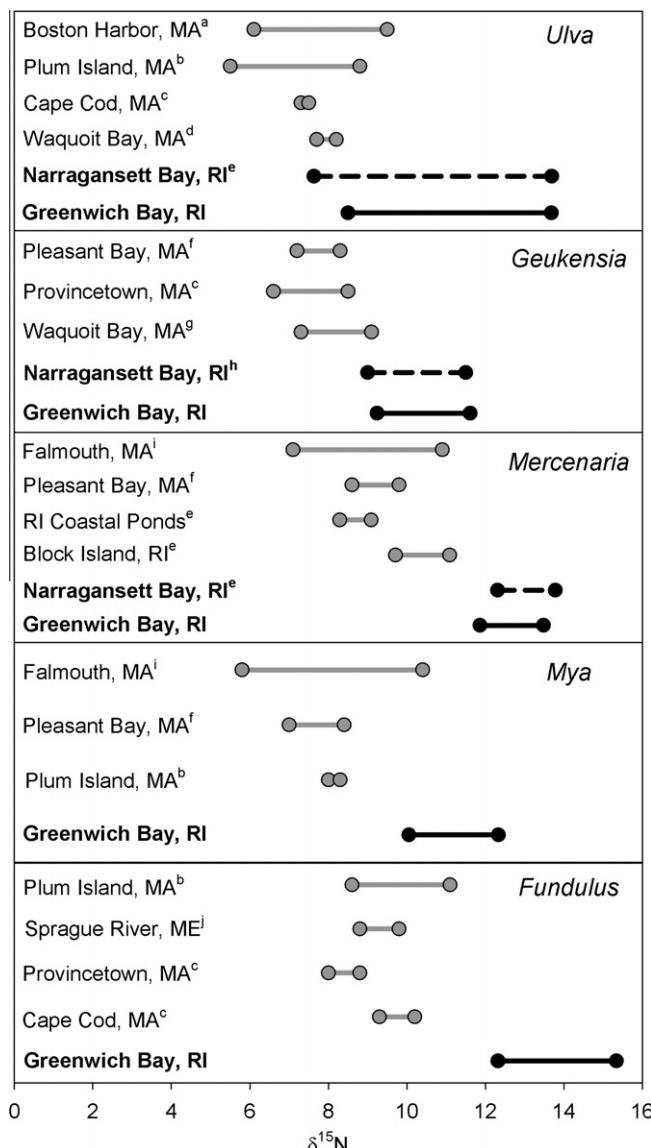
The striking feature of all of the organisms collected over the annual cycle in all parts of Greenwich Bay is their consistent enrichment with isotopically heavy N, with values higher than typically seen elsewhere in New England (Fig. 3). Not surprisingly,  $\delta^{15}\text{N}$  data from primary producers were the most variable (Table 3). Structural morphologies and rapid nutrient uptake rates enable macroalgae like *Ulva* and *Gracilaria* to reflect the isotope signature of ambient DIN in a matter of days (Gartner et al., 2002; Runcie

et al., 2003). Short-term pulses or fluctuations in DIN signatures would not be recorded in organisms with longer tissue turnover times (e.g. tissue N of *Mercenaria* and *Mya* take about 20 days to acquire  $\delta^{15}\text{N}$  values from different food sources; Carmichael, 2004). The typical enrichment across trophic levels was evident and the higher isotope values of *Mercenaria* relative to *Mya* were also observed by Carmichael (2004) working on Cape Cod and result from species-specific filter feeding selection and trophic fractionation.

The lack of spatial differences within the bay indicates that a relatively uniform and heavy N isotope environment characterizes Greenwich Bay. Given the similar  $\delta^{15}\text{N}$  values among the coves and between coves and main stem and the short residence times of the coves (0.3–4.2 days), it appears that the  $\delta^{15}\text{N}$  values of the cove organisms are largely imparted from the main stem rather than from potentially unique watershed inputs to each cove. The DIN results also reflect this homogeneity, where mean  $\delta^{15}\text{NO}_3^-$  and  $\delta^{15}\text{NH}_4^+$  values were similar throughout Greenwich Bay and similar to the surface waters in the upper West Passage of Narragansett Bay.

Our measurements showing that all sources of  $\delta^{15}\text{NO}_3^-$  are relatively low (<8‰) suggests that  $\text{NH}_4^+$  is the major form of DIN supporting the productivity of Greenwich Bay. This is consistent with surveys of nitrate reductase activity by phytoplankton in the upper half of the West Passage of Narragansett Bay and the Providence River estuary by Culver-Rymsza (1988). In 24 surveys over an annual cycle, Culver-Rymsza (1988) found that nitrate uptake and reduction provided less than 10% of phytoplankton N demand in outer Greenwich Bay on 20 sampling dates. Of the ammonium sources, only streams, the wastewater treatment facility (WWTF), and the water of the upper West Passage of Narragansett Bay are marked by isotopically high  $\delta^{15}\text{NH}_4^+$  of >10‰ (Table 1). Further evaluation of the relative importance of these potential sources requires consideration of the magnitude of the source as well as its isotope composition. The three sources of enriched  $\text{NH}_4^+$  (streams, WWTF, and Narragansett Bay) provided approximately  $0.2 \times 10^3$ ,  $0.6 \times 10^3$ , and  $7.1 \times 10^3$  moles  $\text{y}^{-1}$  of  $\text{NH}_4^+$ , respectively (Table 2). If these fluxes are multiplied by the mean  $\delta^{15}\text{NH}_4^+$  of each source (Table 1), the result is a relative mass-weighted isotopic input of about 3% for streams, 8% for the WWTF, and 89% for Narragansett Bay. On an annual basis, it seems clear that the inflow of heavy or enriched  $\text{NH}_4^+$  from Narragansett Bay proper is the major inorganic nutrient source supporting productivity in Greenwich Bay, even during a relatively wet year.

It is possible to carry out a more detailed exercise limiting the calculation to inorganic N contributions and particulate N in phytoplankton during the productive growing season and focusing on an important primary grazer in the system, the quahog or hard clam, *Mercenaria*. As we do not have direct measurements of plankton  $\delta^{15}\text{N}$  values, we use a literature value for the trophic fractionation factor of *Mercenaria* and assume complete phytoplankton draw down of DIN (consistent with summer measurements of DIN in the surface waters of Greenwich Bay; Brush, 2002). We chose *Mercenaria* because of its cultural and economic importance and because its slow tissue turnover time makes it a good long-term integrator of N dynamics (83 days; Carmichael, 2004). As growth in *Mercenaria* is negligible below 10 °C (Pratt and Campbell, 1956), we confine our mass balance to the summer months, when growth rates and nutrient drawdown are greatest (June to September). As precipitation in the Narragansett Bay basin varies little seasonally, annual N fluxes for storm drains and WWTF, as well as volume of wet deposition, were reduced to a quarter (Pilson, 1991).  $\text{NH}_4^+$  and  $\text{NO}_3^-$  concentrations of rainwater were averaged for the period of interest for 2003–2005 (National Atmospheric Deposition Program (NRSP-3), 2011) and characteristic  $\delta^{15}\text{N}$  values for  $\text{NH}_4^+$  and  $\text{NO}_3^-$  (−3.0‰ for both) were taken from the literature (Pardo et al., 2004; Russell et al., 1998). As 14% of annual stream flow in the Narragansett basin occurs June to September, stream



**Fig. 3.** Comparison of literature values of  $\delta^{15}\text{N}$  for select species to values from Narragansett Bay (bold, dashed line) and those from Greenwich Bay obtained during this study (bold line; References: a. Tucker et al., 1999; b. Deegan and Garrity, 1997; c. Wozniak et al., 2006; d. Cole et al., 2005; e. Oczkowski et al., 2008; f. Carmichael et al., 2004; g. McClelland and Valiela, 1998b; h. McKinney et al., 2001; i. Carmichael, 2004; j. McMahon et al., 2005). Sample sizes for organisms collected as a part of this study are listed in Table 3.

and groundwater annual flows were adjusted to reflect this percentage.

Advection from Narragansett Bay during the growing season is approximately  $2.0 \times 10^8 \text{ m}^3$  (Brush, 2002) and we used the Granger et al. (2000) surface water nutrient data from a station just east of Greenwich Bay to estimate concentrations of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  for the summer months (0.8 and 0.2  $\mu\text{M}$ , respectively). As water leaving the Providence River Estuary turns right into the upper West Passage, and a portion of this flow is then diverted into Greenwich Bay, this station should accurately characterize the water being advected into Greenwich Bay (Bergondo, 2004; Kincaid et al., 2008). As phytoplankton productivity is greatest during the summer months, and nutrients are drawn down to 1  $\mu\text{M}$  or less, we estimated the potential N contributions from phytoplankton produced in upper Narragansett Bay and advected into Greenwich Bay. We used chlorophyll-a data reported in Granger et al. (2000) and assumed a carbon to chlorophyll ratio of between 30:1 and 60:1 to estimate phytoplankton carbon (Brush et al., 2002). These values were converted to N using the Redfield Ratio of 106:16 (Redfield, 1958). Our estimated phytoplankton contributions were assigned a  $\delta^{15}\text{N}$  value of 14‰ based on a range of observed values of macroalgae (*Ulva* sp.) measured in the Providence River in the summer of 2005 (13–15‰; Thornber et al., 2008).

The N concentration and flow data from all sources (including Narragansett Bay phytoplankton) were combined to calculate N fluxes. The flux values were used to weight the  $\delta^{15}\text{N}$  values for each source, which, when summed, results in an estimated value of 9‰ (Table 4). With the observed nutrient drawdown in Upper Narragansett and Greenwich Bays during the summer months, this value should reflect the base of the Greenwich Bay food chain (phytoplankton). The value compares well to phytoplankton values (8.9–9.7‰) estimated from the mean  $\delta^{15}\text{N}$  value of *Mercenaria* in the main stem of Greenwich Bay (12.65‰), after accounting for trophic fractionation (3.0–3.8‰; Carmichael, 2004).

The agreement of the  $\delta^{15}\text{N}$  values calculated from our flux weighted isotope budget and those based on measured *Mercenaria* values further support the hypothesis that Upper Narragansett Bay N is largely supporting the Greenwich Bay food web. Of course, the actual  $\delta^{15}\text{N}$  values at the base of the Greenwich Bay food chain are certainly more complicated and dynamic than our simple exercise

suggests. For example, while some of the primary consumers in Greenwich Bay may be directly feeding on Upper Narragansett Bay phytoplankton, some of these phytoplankton may be remineralized and recycled to support new production, presumably with a similar signature (Oczkowski et al., 2010). Fractionations associated with water column or sediment remineralization and recycling, factors not accounted for in the budget, may impact and alter source values. However, despite all of the potential complexities and the assumptions used in our calculations, our results are remarkably consistent with the work of Brush (2002) and Granger et al. (2000).

By our estimates, approximately 55% of the DIN in Greenwich Bay originates from Narragansett Bay. From our isotope mass balance, we can also calculate that about 55% of the isotopic signature in Greenwich Bay *Mercenaria* reflects Narragansett Bay N contributions. While our findings suggest that organisms within Greenwich Bay rely upon autochthonous or near-field watershed sources for some of their N needs, the advected Narragansett Bay water supplies the majority of N to the system and imparts a predominant signature to long-term N integrators in Greenwich Bay. Both the “upside down” N mass balance and the distribution of stable N isotopes in the organisms suggest that nutrient pollution problems in Greenwich Bay will not be resolved by reducing near field watershed sources alone. Greenwich Bay and its small coves are closely coupled by hydrology to the larger system of Narragansett Bay and the much larger N sources that enrich the Providence River estuary.

## 5. Conclusions

Despite varying local contributions of N from the watershed to the coves and main stem of Greenwich Bay, organisms within the bay had remarkably uniform  $\delta^{15}\text{N}$  values, both seasonally and spatially. Organisms throughout Greenwich Bay were characterized by enriched  $^{15}\text{N}$  values that reflected the importance in Greenwich Bay of anthropogenic N discharged into the Providence River estuary from rivers and sewage treatment plants. These far field sources appear to be largely responsible for the productivity of Greenwich Bay. The high productivity of the bay can, in turn, lead to the development of hypoxic and even anoxic events when combined with particular hydrographic and meteorological conditions. The stable isotopic findings are consistent with earlier N input inventories that showed the waters of the upper West Passage of Narragansett Bay as a major path by which reactive N entered Greenwich Bay. The observed “upside-down” N budget for Greenwich Bay contributes to arguments for reducing N discharges from the much larger “upstream” sewage treatment plants, including that of the City of Warwick that discharges to the Pawtuxet River (Fig. 1). Since this study was completed, all three of the WWTFs that discharge to the Pawtuxet River have been upgraded to remove N, but the impact of this development on the N budget of Greenwich Bay has not yet been quantified.

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**Table 4**

Nitrogen stable isotope budget calculated for Greenwich Bay over the growing season (June to September). Narragansett Bay is abbreviated to Narr. Bay and phytoplankton to phytopl.

Source	Flow ( $10^6 \text{ m}^3$ )	N	$\delta^{15}\text{N}$ (‰)	Conc. ( $\mu\text{M}$ )	Flux ( $10^4 \text{ mol}$ )	Weighted $\delta^{15}\text{N}$
<i>Watershed sources</i>						
Groundwater	1.2	$\text{NH}_4^+$	2	12.4	1	0.0
		$\text{NO}_3^-$	5	279	33	0.5
Storm drains	0.7	$\text{NH}_4^+$	3	48	3	0.0
		$\text{NO}_3^-$	8	279	20	0.5
Streams	3.5	$\text{NH}_4^+$	12	9.2	3	0.1
		$\text{NO}_3^-$	7	169	59	1.3
WWTF	0.5	$\text{NH}_4^+$	11	288	14	0.5
		$\text{NO}_3^-$	7	422	21	0.5
<i>Allochthonous sources</i>						
Narr. Bay	202.7	$\text{NH}_4^+$	11	0.8	16	0.6
		$\text{NO}_3^-$	2	0.2	4	0.0
		Phytopl.	14 <sup>a</sup>	6 <sup>a</sup>	122	5.5
Rain	4.0	$\text{NH}_4^+$	-3	9.6	4	0.0
		$\text{NO}_3^-$	-3	17	7	-0.1
		Sum:			308	9
		Measured:				8.9–9.7 <sup>b</sup>

<sup>a</sup> Phytoplankton values are estimated to range from 13‰ to 15‰ and concentration to range from 4.0 to 8.1  $\mu\text{M}$ .

<sup>b</sup> The average value for *Mercenaria* from the main stem of Greenwich Bay minus a trophic fractionation ranging from 3.0‰ to 3.8‰.

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