Salt marsh tidal exchange increases residence time of silica in estuaries

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Abstract

   We present flux measurements of dissolved silicon (DSi), biogenic Si (BSi), and dissolved inorganic nitrogen (DIN) and phosphorus (DIP) on a temperate salt marsh in Narragansett Bay, Rhode Island, over neap, mid, and spring tide cycles during the spring and the summer seasons to determine the stoichiometry of marsh tidal export and the potential effect on Si availability in the receiving estuary. During the spring, when incoming waters were depleted in DSi (average 1.7 μmol L^{-1}), the marsh was a net sink of BSi (132 mol h^{-1}) and a source of DSi (31 mol h^{-1}) to the estuary. During this period, the DIN : DSi ratio of ebbing water was more than five times lower than that of flood water. Together, these data indicate that marsh nutrient fluxes "outwell" nutrients in ratios that support spring diatom growth in Narragansett Bay. However, during the entire sampling period the marsh served as a net sink for both DSi and BSi, importing, on average, 14 mol DSi h^{-1} and 86 mol BSi h^{-1}. We hypothesize that the net import and retention of Si by salt marshes provides a previously overlooked ecosystem service of increasing the residence time of Si in estuarine systems. In the absence of salt marshes, we calculate that 5.1×10^4 kmol of Si would be exported from the estuary during the growing season, decreasing the availability of Si in the system and having direct repercussions for phytoplankton species composition in nearby estuarine waters.

   Diatoms are one of the most prolific groups of phytoplankton in marine waters, both globally and in temperate systems (Smayda 1998; Irigoien et al. 2002). The abundance of diatoms in marine waters has important implications for marine ecology, because diatoms are the preferred food source for higher trophic organisms and are often more nutritious than other types of phytoplankton (Irigioen et al. 2002). In addition, diatoms are more efficient than most other phytoplankton at exporting fixed carbon (C) to the benthos (Ittekkot et al. 2000). As such, diatom abundance in marine waters has important implications for marine ecology and global C cycling.

   Unlike most other types of phytoplankton, diatoms require as much silicon (Si) as nitrogen (N) to survive on a molar basis (Redfield et al. 1963). Thus, the amount of Si relative to the macronutrients N and phosphorus (P) in coastal waters is one important factor dictating whether diatoms will proliferate. Until recently, the amount of dissolved Si (DSi) in marine systems was thought to be controlled primarily by geochemical factors, such as weathering rates and climate (Bluth and Kump 1994). Whereas this is true on the global scale, human activities have also been shown to affect Si availability in coastal waters at the regional scale. For example, agricultural runoff and fossil fuel combustion have increased exports of N and P relative to Si to downstream receiving waters, thus altering nutrient ratios in aquatic systems. During conditions of excess N and P relative to Si, diatoms will bloom until no more Si is available, inducing Si-limited conditions in which nondiatom species bloom (Conley et al. 1993;

Anderson et al. 2002). Similarly, lakes and impoundments trap larger quantities of Si relative to N and P, often resulting in Si limitation downstream of reservoirs and lakes (Van Bennekom and Salomons 1981; Humborg et al. 2008). Further, land-use change is another means by which human activities have disrupted the global Si cycle. Because large quantities of Si are found in terrestrial plants and soils, changes in land use or land cover can alter the amount of Si retained in the terrestrial biosphere and exported to aquatic systems (Struyf et al. 2010; Clymans et al. 2011; Carey and Fulweiler 2012). The recent recognition that humans can alter the global Si cycle has led to further questions about the controls on the fate and transport of the element in the biosphere.

   Weathering of the lithosphere is the ultimate source of DSi, and rivers are the major vectors of large-scale redistributions of Si between continents and the ocean, transporting large quantities ($\sim$ 6 Tmol) to marine waters each year (Tréguer and De La Rocha 2013). In fact, rivers supply $\sim$ 80% of Si imported into the global ocean each year (Tréguer and De La Rocha 2013). However, the pathway of Si from rocks to rivers to oceans is not direct, due to the dynamic nature of Si biogeochemistry at the land–sea interface. For example, at the intersection of terrestrial and marine environments lie tidal wetlands, which play an important role in Si exchange (Struyf et al. 2006; Vieillard et al. 2011). Large quantities of Si are found in tidal wetlands, including wetland grasses, sediment, and pore water (Struyf et al. 2005*b*; Carey and Fulweiler 2013*a*). Like diatoms, wetland grasses take up DSi, forming biogenic Si (BSi) within their tissue. BSi is typically concentrated at transpiration termini of the plant, such as leaves of grasses (Epstein 1994). Compared to mineral silicates, BSi is rapidly recycled, being orders of magnitude more soluble than mineral silicates (Conley 1997; Cornelis

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et al. 2011). Similar to marsh grasses, wetland sediments are also rich in Si, specifically amorphous Si (ASi), which includes BSi and pedogenic silicates, such as precipitated opal or Si sorbed to oxide minerals (Sauer et al. 2006; Cornelis et al. 2011).

In addition to being large reservoirs of Si, wetlands are places of rapid Si transformation, recycling Si between the various portions of the marsh (Struyf et al. 2005a; Carey and Fulweiler 2013a). Because of their ability to recycle Si from one form to the other, tidal wetlands have been shown to regulate the fluxes of Si to the adjacent estuary (Struyf et al. 2006; Vieillard et al. 2011). Tidal wetlands (both fresh- and saltwater wetlands) typically serve as sinks of BSi and as sources of DSi to adjacent waters (Struyf et al. 2006; Vieillard et al. 2011). However, recent flux estimates from the Walden Sea point toward the marsh being a net sink of Si, with marsh age and management activities (i.e., grazing) exerting potential controls over Si cycling (Müller et al. 2013a,b). Thus, the role of wetlands in regulating Si fluxes to downstream receiving waters remains uncertain. Moreover, not only is the form (BSi vs. DSi) and magnitude of Si exchange important in tidal marshes, but the molar ratios of N : P : Si are also relevant because they help to determine phytoplankton species composition. Although a study of N : P : Si fluxes in a freshwater marsh was recently completed (Van Damme et al. 2009), to our knowledge, no studies have yet examined the stoichiometry of salt marsh nutrient (N : P : Si) fluxes.

The purpose of this research was twofold. We wanted to determine the role of temperate salt marshes in regulating Si exchange with the adjacent estuary. Additionally, we wanted to compare the stoichiometry of marsh export fluxes (N : P : Si) in order to understand how salt marshes influence nutrient ratios of coastal waters. To do this, we quantified the net fluxes of dissolved inorganic nitrogen (DIN), dissolved inorganic phosphate (DIP), DSi, and BSi from a relatively undisturbed salt marsh in southern New England over six complete tidal cycles during the spring and summer seasons of 2011.

Methods

We measured salt marsh fluxes at Nag Marsh, located on the Narragansett Bay National Estuarine Research Reserve (NBNERR; Fig. 1) in Rhode Island. Water movement through the marsh occurs through a single tidal creek, making marsh nutrient flux calculations possible. The 0.12 km² marsh has classic vegetation zonation patterns typical of New England marshes, with *Spartina alterniflora* being found in the low-marsh and *Spartina patens* dominating the high-marsh platform (Bricker-Urso et al. 1989). Due to its protected nature, this site has been used in numerous studies to represent a relatively undisturbed temperate North American salt marsh (Wigand et al. 2004a,b; Carey and Fulweiler 2013a). In fact, an inventory of net Si accumulation was recently completed for this marsh, which quantified the amount of Si found in the marsh pore water, sediment, and above- and belowground vegetation seasonally for 1 yr (Carey and Fulweiler 2013a).

In order to calculate fluxes (mass of Si per unit time), both concentration and discharge (water flow per unit time)
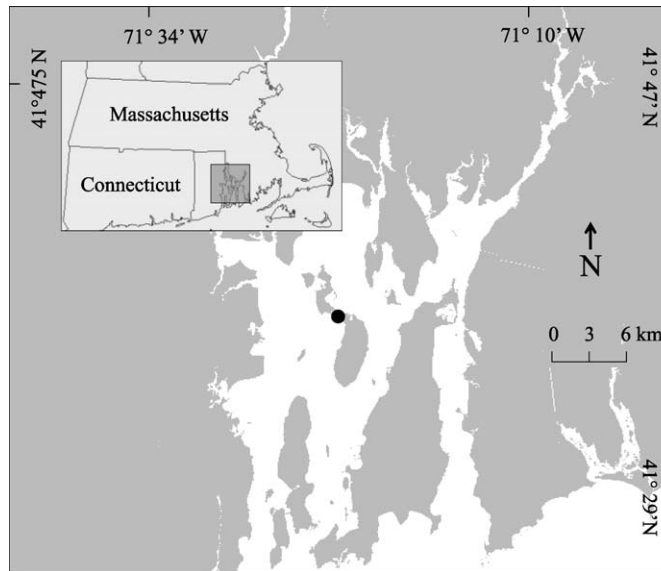

Fig. 1. Map of Nag marsh located on the Narragansett Bay National Estuarine Research Reserve (NBNERR) in Narragansett Bay, Rhode Island.

data are needed. We measured concentrations of nutrients once per hour during six complete 13 hr tidal cycles—a neap, mid, and spring tide during both the active growing season (May 2011) and during peak biomass (August 2011; $n = 78$). We collected creek samples using an Isco automatic water sampler hourly from sundown to sunrise ($\sim$ 18:00 h to $\sim$ 07:00 h) on all occasions. Samples were kept on ice overnight; and in the morning they were filtered using a 60 mL polypropylene syringe, a 0.40 micron polycarbonate filter for DSi, and a 0.45 micron glass fiber filter (Whatman GF/F) for DIN and DIP. The polycarbonate filter was saved and frozen for subsequent BSi analysis. DIN and DIP samples were frozen until laboratory analysis, whereas DSi samples were not frozen but were kept in a cool, dark environment. We also measured total suspended solid (TSS) concentrations in tidal creek water by filtering 150 mL of water through a precombusted (400°C for 4 h) Whatman GF/F filter; these were placed in a drying oven at 60°C until dry. All samples were taken in duplicate.

We measured BSi concentrations using the wet chemical alkaline extraction technique and 1% Na_2CO_3 solution, with samples subsampled at hours 3, 4, and 5 in order to determine the mineral silicate correction factor (Conley and Schelske 2001; Sauer et al. 2006). We used a Seal Analytical flow injection analyzer to measure concentrations of nutrients (DIN, DIP, DSi, and BSi [post alkaline digestion]). DSi was determined using the blue molybdate method and sodium hexafluorosilicate (Na_2SiF_6) as the silicate standard (Strickland and Parsons 1968). DIN was measured using cadmium reduction followed by colorimetric determination of nitrite, and DIP was measured by the ascorbic acid method (Strickland and Parsons 1968).

We measured tidal flow, or discharge (Q), at the inlet of the marsh site using a Marsh McBirney velocity (V) meter and measuring cross-sectional area (A) of the creek channel
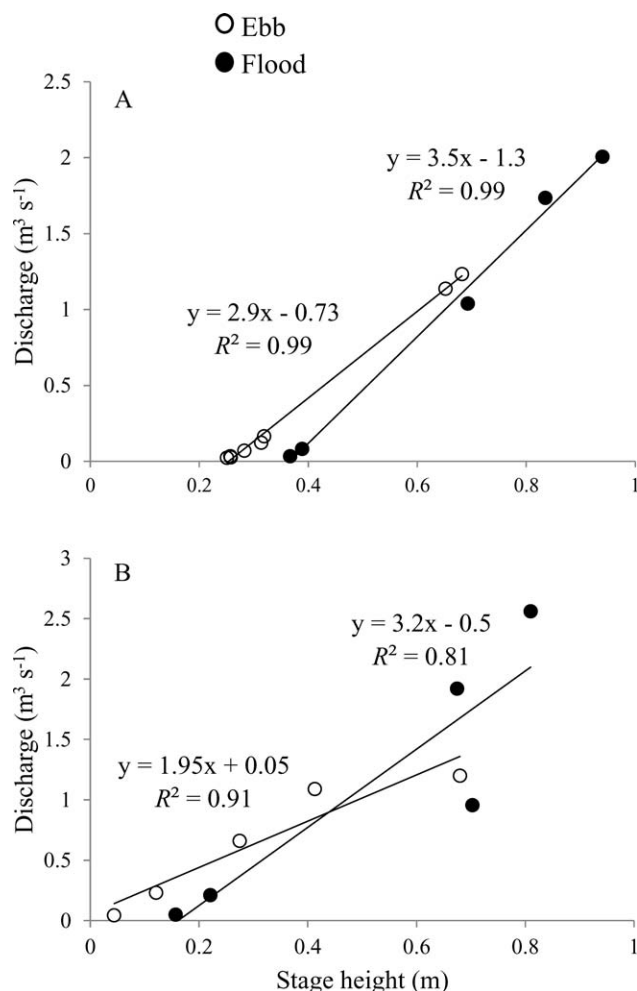
Fig. 2. Rating curves for ebb and flood tides in the (A) spring and (B) summer periods.

(Q = V × A). We developed four unique rating curves, which relate stage height (i.e., water level) to discharge, one each for the incoming and outgoing tides during both the spring and summer sampling periods (Fig. 2). Creating separate curves for incoming and outgoing tides is most accurate, as velocities at the same water level are not equal for the flood and ebb tides, and it is possible that cross-sectional channel area changed between spring and summer sampling periods. Each of the four rating curves was developed with at least five measurements using linear regressions between stage and discharge, with a total of 23 stage–discharge measurements. Goodness of fit (coefficient of determination, or R^2) was over 0.90 for all curves, except the summer incoming curve, for which $R^2 = 0.81$ (Fig. 2). The discharge measurements used to build the curves were taken throughout the range of tidal heights observed in our creek (0.04 m to 0.94 m), so that the range of tidal heights and associated discharges were well represented. We used an Onset Hobo water level logger to record water level every 5 min during the tidal cycles in order to determine discharge for every time point when concentration data were calculated. Discharges were considered zero if an hourly sample was taken during slack tide.

We calculated the fluxes of nutrients coming in and out of the marsh for each complete tidal cycle by multiplying concentrations by discharge ($n = 13$ for each of the six tidal cycles), resulting in a total of 78 flux measurements used in this study. Flooding tides (incoming) received positive values and ebbing (outgoing) tides were given negative values. Rather than extrapolating between measurements, flux values for each tidal cycle were integrated, or summed, in order to determine the net flux of Si through the marsh during each cycle (Fig. 3; Table 3; Vieillard et al. 2011).

Results

Creek discharge—Throughout the study, discharge in the creek ranged from zero to 2.02 m^3 s^{-1}, and average flows were nearly equal during both sampling seasons (average 0.05 ± 0.13 m^3 s^{-1} in both seasons). Except for the summer neap tide, when total inflows nearly equaled outflow (1.2×10^4 m^3 in both cases), water movement through the marsh creek was slightly imbalanced, with more water entering than leaving the marsh in every tidal cycle; on average, 1.2 times (range of 1.1 to 1.3 times) more water entered the marsh than was exported (Table 1). No seasonal differences were observed in these imbalances (Tables 1, 2). The tidal range was 0.9 m, and the average salinity of the tidal creek water was 27.6.

Nutrient concentrations—Across all tidal cycles, spring DSi concentrations (0–26 μmol L^{-1}) were lower than summer DSi concentrations (23–56 μmol L^{-1}), whereas spring BSi concentrations (14–53 μmol L^{-1}) were typically higher than summer BSi concentrations (4–27 μmol L^{-1}; Table 2). NH$_4^+$ was the predominant DIN species found in the tidal creek water, being an order of magnitude higher than NO$_x$ (NO$_2^-$ + NO$_3^-$) concentrations in the summer and two orders of magnitude greater in the spring (Table 2). Spring DIN and DIP concentrations ranged from 0.7 μmol L^{-1} to 3.5 μmol L^{-1}, and 0.06 μmol L^{-1} to 1.3 μmol L^{-1}, respectively, whereas summer DIN and DIP concentrations were higher, ranging from 1.3 μmol L^{-1} to 13 μmol L^{-1} (DIN) and 0.8 μmol L^{-1} to 3.3 μmol L^{-1} (DIP).

Stark differences in the chemical signatures of flooding and ebbing tides were observed during the spring (Table 2), likely due to mixing of different sources of water in the creek. Spring flood waters contained an order of magnitude less DSi than outgoing flows (1.7 μM vs. 12.5 μM). As a result of the DSi-depleted flood waters, the DSi-rich creek water showed a dilution pattern during the incoming tides, with higher discharge associated with lower concentrations. Such a pattern is governed by changing sources of water, specifically DSi-rich water leaving the marsh with DSi-depleted estuarine surface water entering the marsh (Fig. 2A,E). However, this pattern did not occur during the summer mid and neap tides, when ebb and flood waters had roughly equal concentrations of DSi (Fig. 3E; Table 2). Although BSi concentrations were almost 40% larger in incoming vs. outgoing flows (26 μmol L^{-1} vs. 18 μmol L^{-1}) in the spring (Table 2), BSi concentrations did not exhibit strong relationships between concentration and discharge in either season (Fig. 3B,F).
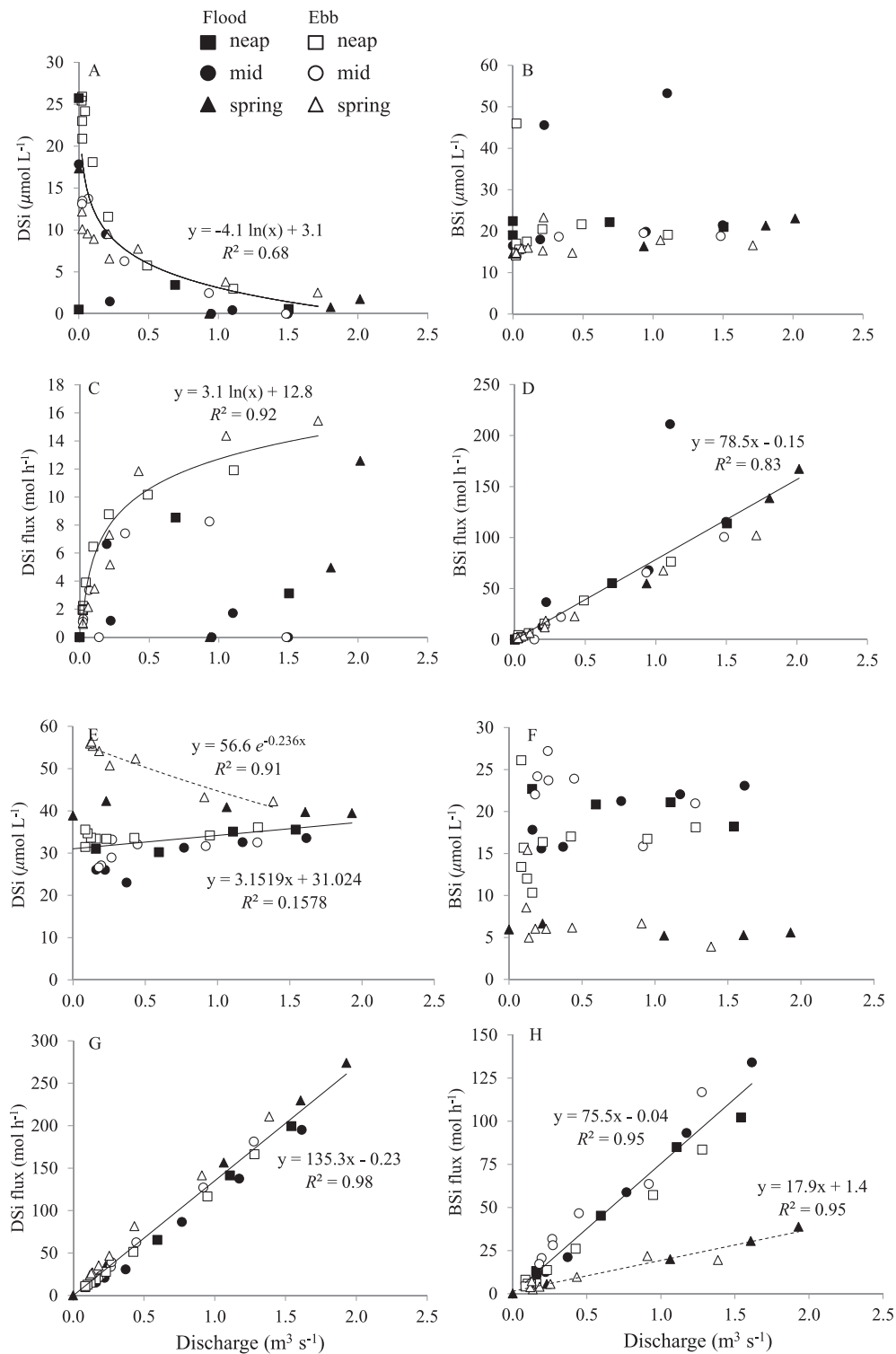
Fig. 3.   Dissolved silica (DSi, as H_4SiO_4; A, E) concentration, (B, F) flux, (C, G) biogenic silica (BSi) concentration, and (D, H) BSi flux as a function of creek discharge during the (A–D) spring and (E–H) summer. Only significant trend lines and fits shown, which includes the following tides (A) all ebbing data together, (C) spring and mid ebbing tides, (D) all data together. (E) Spring tide ebbing (dashed), all other data together (solid), (G) all data together, (H) spring tide ebbing and flooding (dashed), all other data together (solid).

Table 1. Total volume of water imported and exported through tidal creek during each tide.

	Flood tide (m³)	Ebb tide (m³)
Spring		
Neap	7.90×10^3	7.37×10^3
Mid	1.43×10^4	1.08×10^4
Spring	1.71×10^4	1.38×10^4
Average	1.31×10^4	1.07×10^4
Summer		
Neap	1.23×10^4	1.24×10^4
Mid	1.56×10^4	1.28×10^4
Spring	1.74×10^4	1.28×10^4
Average	1.51×10^4	1.26×10^4
Average both seasons	1.41×10^4	1.17×10^4

Similar to DSi, average DIN and DIP concentrations of ebbing water were higher (1.2 and 2.7 times, respectively) than flooding waters during the spring. DIP concentrations also exhibited evidence of mixing of different water sources in all tidal cycles, with the lowest concentrations measured at high tide and the highest concentrations measured at low tide. In contrast, DIN concentrations only demonstrated this relationship during the summer spring-tide sample period.

TSS concentrations ranged from 4 mg L^{-1} to 33 mg L^{-1} (average 9.5 ± 1 mg L^{-1}) in the spring and 4 mg L^{-1} to 16 mg L^{-1} (average 7.8 ± 0.4 mg L^{-1}) during the summer. Spring inflows had higher TSS concentrations (11.6 mg L^{-1}) compared to outflows (8.7 mg L^{-1}), but no differences between the incoming and outgoing flows were observed in the summer. BSi concentrations were positively correlated to TSS concentrations only during the neap tide during the summer ($R^2 = 0.51$).

Nutrient fluxes—Incoming fluxes were given positive values and outgoing fluxes negative values, so that the sign (negative or positive) of the integrated creek fluxes over a tidal cycle indicates whether the marsh was serving as a net source or sink for nutrients. Overall, including both dissolved and biogenic spring and summer Si fractions, the marsh served as a net sink for Si, importing an average of 14 mol h^{-1} and 86 mol h^{-1} of DSi and BSi, respectively (Table 3). However, there were clear differences between Si species, as well as strong seasonal variability. For example,

whereas BSi was consistently imported into the marsh during both seasons (an average of 132 mol h^{-1} and 39 mol h^{-1} in the spring and summer, respectively), the directions of DSi fluxes were seasonally dependent. During the spring, the marsh served as a net source of DSi to the estuary, exporting 31 mol h^{-1}; whereas, during the summer, the marsh imported 59 mol h^{-1} on average (Table 3). BSi fluxes were elevated compared to DSi fluxes in the spring, likely due to DSi uptake and BSi production by diatoms in the estuary.

On average, the marsh was a net source of DIN and DIP to the estuary, exporting 7.7 mol h^{-1} and 1.8 mol h^{-1}, respectively (average both seasons; Table 3). Similar to fluxes of Si, species and seasonal differences in DIN fluxes were observed. Over an order of magnitude more DIN was transported through the tidal creeks during the summer (an export of 16.5 mol h^{-1}) compared to the minor sink observed during the spring (1.2 mol h^{-1}). Similarly, DIP exports were more than double in the summer (average 2.4 mol h^{-1}) compared to the spring (1.1 mol h^{-1}). Although net NH$_4^+$ and NO$_x$ fluxes were always in the same direction, NH$_4^+$ accounted for the majority of DIN fluxes (60–100%; Table 3).

Discussion

Water balance—Except for the neap tide in the summer, more water came into the marsh than left in every case (Table 1). It is not unusual for water discharge on the relatively short time scale of one tidal cycle (~ 13 h) to be unbalanced (i.e., inflow does not equal outflow; Nixon 1980; Struyf et al. 2006; Vieillard et al. 2011). The fate of this "extra" water entering the marsh is likely losses through evapotranspiration, ponding on the marsh surface, and infiltration into marsh sediment. Vertical seepage, or infiltration, during the flood tide is a well-recognized means of restoring water to sediments, as pore water drains the marsh during the low tide and needs replenishment (Childers et al. 2002; Vieillard et al. 2011).

Nutrient fluxes: A case for "outwelling"?—Measuring net fluxes of nutrients between a salt marsh and an adjacent estuary allows us to address the concept of "outwelling." Originally proposed by J. Teal in 1962 and later by E. P. Odum in 1968, the Outwelling Hypothesis refers to the ability of marshes to supply nutrients necessary for primary

Table 2. Average concentrations, molar ratios, and discharge (Q) in flood and ebb tides. Ebb and flood tides had different Si concentrations during the spring but not in the summer. During both seasons, DIN and DIP concentrations were lower on the flooding tides. Average flooding discharges were always higher than ebbing.

	DSi (µmol L^{-1})	BSi (µmol L^{-1})	NH$_4^+$ (µmol L^{-1})	NO$_x$ (µmol L^{-1})	PO$_4^{3-}$ (µmol L^{-1})	N : P	N : Si	Q (m³ s^{-1})
Spring								
Flood tide	1.7	26.8	1.0	0.08	0.2	4.42	0.65	0.99
Ebb tide	12.5	18.2	1.5	0.01	0.7	2.22	0.12	0.32
Summer								
Flood tide	33.7	15.1	5.1	0.3	1.3	4.17	0.16	0.82
Ebb tide	38.7	15.1	7.3	0.5	1.9	4.04	0.20	0.44

Table 3.   Fluxes of nutrients (DSi, BSi, DIN, DIP) and ratios of the export. Negative fluxes indicate a net export of material. Positive fluxes indicate a net import of material. N : P ratios less than 16 indicate a N-limited system. N : Si ratios greater than one indicate Si limitation. Dashes indicate values not applicable due to net fluxes in different directions.

	Net flux (mol h^{-1})						Nutrient export ratios	
	DSi	BSi	NH$_4^+$	NO$_x$	DIN	DIP	N : P	N : Si
Spring								
Neap	−37.6	22.1	−2.9	0.0	−2.9	−1.9	1.5	0.1
Mid	−11.9	248.8	4.5	2.2	6.7	0.5	12.8	—
Spring	−44.1	126.0	−0.3	<0.01	−0.3	−2.1	0.2	0.01
Average	−31.2	132.3	0.4	1.1	1.2	−1.1	4.8	—
Summer								
Neap	−9.9	33.3	−39.5	−3.6	−43.0	−6.0	7.2	4.4
Mid	83.8	62.4	−9.2	−2.2	−11.4	0.5	—	—
Spring	102.6	21.3	3.3	1.6	4.9	−1.9	—	0.05
Average	58.8	39.0	−15.1	−1.4	−16.5	−2.4	6.7	—
Average both seasons	13.8	85.6	−7.3	−0.1	−7.7	−1.8	4.3	—

and secondary production in estuaries. The several existing reviews of flux studies (Nixon 1980; Childers et al. 2002) have been unable to definitively reject or accept the Outwelling Hypothesis, but a general trend for the marsh to import organic matter and export inorganic matter has been noted (Nixon 1980).

Our DIN and DIP data support this hypothesis. Although we do not have organic N or P values, we do observe an export of NH$_4^+$ and DIP (Table 3). The marsh served as a net source of DIN to estuarine waters during four of the six tidal cycles, mostly due to ammonium fluxes. Ammonium fluxes have been found to be the major form of DIN exported from New England marshes in prior studies (Valiela et al. 1978), likely due to organic matter remineralization (Valiela et al. 1978) and high denitrification rates, which consume available NO$_3^-$. Scaling up a recently measured New England salt marsh denitrification rate (71.3 μmol N m^{-2} h^{-1}; Koop-Jakobsen and Giblin 2010) to the marsh studied here, we calculate a removal rate of up to 8.1 mol N h^{-1}, which may explain why ebbing NO$_x$ concentrations were eight times lower than flooding water on average during the spring (0.08 μmol L^{-1} vs. 0.01 μmol L^{-1} in flood vs. ebbing water).

Compared to examination of the "outwelling" concept with respect to carbon, N, and P cycling, relatively little attention has thus far been paid to the "outwelling" of Si in estuarine environments. Although Hackney et al. (2002) hypothesized that salt marsh Si dynamics fuel secondary production in estuarine systems through benthic diatom production on marsh surfaces, they did not test this hypothesis directly, because no fluxes of DSi or BSi were reported (Hackney et al. 2002). However, three salt marsh studies have reported both organic (BSi) and inorganic (DSi) fluxes (Struyf et al. 2006; Vieillard et al. 2011; Müller et al. 2013a). Our spring data match the trend found in two of these studies (Struyf et al. 2006; Vieillard et al. 2011), with the estuary studied here importing BSi (132 mol h^{-1}) into the marsh and exporting DSi (31 mol h^{-1}) from the marsh (Table 3). This pattern provides support for the idea that salt marshes may "outwell" DSi. However, our

summer data show a different pattern, with a net import of both DSi (59 mol h^{-1}) and BSi (39 mol h^{-1}) fractions (Table 3), which continues to call the "outwelling" hypothesis into question. The average net import of DSi during the summer is likely due to the relatively elevated DSi concentrations in flood waters that typically result from BSi remineralization during warmer summer months in temperate estuaries (Yamada and D'Elia 1984; Carbonnel et al. 2013), in addition to the larger net inflow of water into the marsh during the summer spring and mid tides (Table 1).

Averaging our values for the entire sampling period for both DSi and BSi, we find that the marsh is a net sink of Si (99 mol h^{-1}; Table 3), with roughly three times more Si imported into the marsh compared to exports on average. These results align with a recently published report of salt marsh Si budgets from the Wadden Sea (Germany), which also finds the salt marsh to serve as a net sink of Si, mostly due to large BSi imports (Müller et al. 2013a). The deposition of BSi on the marsh surface, retention of BSi by marsh grasses, and slow DSi remineralization likely contribute to the marsh serving as a net Si sink. Müller et al. (2013a) suggest that storm events provide large net imports of Si into marshes and that exclusion of storm events from flux studies may underestimate the role of salt marshes in retaining Si. Because we did not measure fluxes during a storm event, our estimates regarding the degree to which salt marshes may serve as a net Si sink may be conservative.

We did not measure net Si fluxes during the fall and winter seasons, making annual flux estimates difficult. Because we observe a net BSi import in all six of our tidal cycle measurements, we hypothesize that a similar pattern holds true during the fall and winter seasons, especially since strong fall and winter storms could deposit large amounts of BSi on the marsh platform during this period. However, BSi imports will also vary depending on the timing and intensity of the winter–spring diatom bloom, which has been shown to be highly variable in recent decades (Nixon et al. 2009). With regard to estimating DSi

fluxes during the fall and winter, published pore-water DSi concentrations from this marsh show concentrations that are maximum during the spring and decline throughout the year, reaching minimum values in the winter (Carey and Fulweiler 2013*a*). Based on this pattern and the idea that DSi fluxes are governed mostly by pore-water seepage (Vieillard et al. 2011; Müller et al. 2013*a*), we would expect DSi concentrations that are higher during the spring and that decline through the summer. However, we did not observe this pattern (Table 2), leading us to conclude that concentrations of DSi in flood waters are also critical in determining net DSi fluxes. DSi concentrations in Narragansett Bay's water column are usually highest during the winter, with minimums during the early spring (Smayda and Borkman 2008), aligning with our observations of lower DSi concentrations during spring season flood waters compared to the summer (Table 2). In turn, the marsh may serve as a DSi sink during the fall and winter seasons. Nevertheless, it is clear that large uncertainties remain over fall and winter Si fluxes, and further experiments are needed to examine annual marsh Si fluxes.

Si fluxes: Regional comparisons—We find it most useful to compare our results to those of Vieillard et al. (2011) because both studies were done in the same region (New England) on salt marshes with the same type of vegetation (dominated by *Spartina*). Despite these similarities in marsh characteristics, differences in Si behavior between the two marshes are apparent, specifically regarding the magnitude and directions of the fluxes. Vieillard et al. (2011) measured DSi and BSi fluxes during the summer period only, and they observed a net export of DSi from the marsh and a net import of BSi. In contrast to Vieillard et al. (2011), our summer flux measurements document an import of DSi into the marsh (summer average of 59 mol h^{-1}; Table 3). Further, the BSi and DSi concentrations observed in Nag marsh were lower than those found in the Vieillard et al. (2011) study, as our maximum observed Si concentrations (56 μmol L^{-1} DSi and 27 μmol L^{-1} BSi) were roughly half that of Vieillard et al. (2011; 108 μmol L^{-1} DSi and 56 μmol L^{-1} BSi). We hypothesize that the lower Si availability in our marsh may be due to the higher proportion of sandy course sediments in our system compared to the Vieillard et al. (2011) study. Because of these differences in concentrations, and the smaller tidal prism of our marsh, the Vieillard et al. (2011) study calculated a much higher average DSi flux (169 mol h^{-1}) compared to our average DSi fluxes (31 mol h^{-1} and 59 mol h^{-1}, in the spring and summer, respectively; Table 3). Both studies did observe tight correlations between summer Si fluxes (both BSi and DSi) and creek discharge, highlighting that water movement through the creek is a larger driver of Si fluxes in the marsh than are Si concentrations.

We compared our spring DSi exports to the summer exports reported by Vieillard et al. (2011), as springtime was the only season in which we observed net DSi exports from the marsh. In examining DSi concentrations as a function of creek discharge during the spring, we observe that our marsh also serves as a "point source" of DSi to the adjacent estuary, denoted by negative logarithmic slope of the regression between these two variables ($R^2 = 0.68$; Fig. 3A). Such a pattern is governed by different sources of water, namely smaller volumes of DSi-rich water mixing with larger volumes of DSi-depleted surface waters. Normalizing our spring flux value by the area of the tidal creek (0.115 km^2), we calculate a spring flux (90 d) of 586 kmol km^{-2}, a value that is ~ 60-fold higher compared to values reported by Vieillard et al. (2011; 9.2 kmol km^2 over the 90 d). Given the higher concentrations and fluxes documented in the Vieillard et al. (2011) study, this discrepancy was initially surprising. However, these differences in the area-normalized fluxes are a result of Vieillard et al. (2011) being conservative in the values they used as the area of their marsh. Vieillard et al. (2011) normalized (divided) their flux by the entire area of the Great Marsh (40 km^2), rather than the unknown area of the much smaller area inundated by tidal creek water in their study. Thus, the area-normalized fluxes reported in Vieillard et al. (2011) are likely two to three orders of magnitude higher than reported.

Stoichiometry of marsh–estuarine nutrient exchange— Examining the stoichiometry of marsh exports allows us to assess the role of marsh–estuarine exchange in supplying nutrients for primary production in the adjacent estuary, Narragansett Bay. Nutrient ratios of N : P < 16 indicate potential N limitation (Howarth et al. 2011). Our data show that ratios of N : P were consistently < 16 (Tables 2 and 3), agreeing with prior work showing Narragansett Bay to be N limited (Smayda and Borkman 2008). Because it is a N-limited system, the ratios of N : Si (rather than P : Si) are important controls over whether or not diatoms can bloom. Diatoms are the most dominant form of phytoplankton in Narragansett Bay (Smayda and Borkman 2008), requiring as much Si as N on a molar basis (Redfield et al. 1963). As such, N : Si ratios < 1 indicate that more than enough Si is being supplied to the marsh for diatom production. In all of the spring tidal cycles, the marsh exported Si and N in proportions that support diatom growth (Tables 2, 3), aligning with results from a freshwater tidal Si flux study (Van Damme et al. 2009). In turn, we propose that the relatively large quantities of DSi relative to DIN exported from the marsh during the spring likely play an important role in encouraging diatom production in the estuary. This hypothesis is supported by the differences in N : Si ratios in ebb and flood waters during the spring, with N : Si ratios of ebb water being more than five times lower than flood waters (Table 2). The Si-depleted flood waters during the spring (average DSi concentrations of 1.7 μmol L^{-1}; Table 2) highlight the low Si concentrations in the Bay during this period.

In the summer, the implications of N : Si fluxes are less clear, as N : Si ratios of both greater and less than one were observed, in addition to net fluxes in of DSi and DIN in opposite directions (i.e., imports of DSi and exports of DIN; Table 3). Although the marsh did not supply more Si compared to N in two out of the three summer tidal cycles measured, this likely does not hinder diatom growth in the estuary because DSi appears not to be limiting during this

period, as indicated by average N : Si ratios of 0.16 of incoming flood waters (Table 2) and elevated DSi concentrations in the water column during the summer period (Smayda and Borkman 2008). Average summer N : Si ratios were similar in both ebb and flood tidal cycles (0.2 and 0.16, respectively), neither of which indicates Si limitation (Table 2).

Implications for ecosystem services—Rivers are well known to supply the vast majority of DSi to marine waters ($\sim 80\%$ annually; Tréguer and De La Rocha 2013). During the same year that we measured marsh nutrient fluxes (2011), four nearby rivers in southern New England had an average spring DSi flux of 115 mol d^{-1} km^{-2} (Carey and Fulweiler 2013*b*). We compared this value to our spring period when we observed marsh DSi export (6.5 $\times$ 10^3 mol d^{-1} km^{-2}), finding that the salt marsh exported an order of magnitude more DSi to the downstream receiving waters during the spring. Considering that this is the period when the estuarine water was depleted in DSi and that river DSi fluxes can be at a minimum (Fulweiler and Nixon 2005; Carey and Fulweiler 2013*b*), we hypothesize that northeastern U.S. salt marshes play an especially important role in supplying DSi to marine waters during this highly productive period.

Just as marsh DSi export provides an important ecosystem service, we argue that the opposite process of Si import is also critical. Expanding on the idea that tidal marshes act as a "leaky dam" (Yelverton and Hackney 1986), we propose that tidal marshes act as a Si sponge, storing Si for a period of time and often transforming Si from organic to inorganic before release to estuarine systems. In turn, we hypothesize that salt marshes increase the residence time of Si in northeastern estuaries. In the absence of salt marshes, our data suggest that Si would be more rapidly exported from Narragansett Bay, rather than being deposited on marsh surfaces and recycled for subsequent reuse by biological organisms.

In order to approximate how much Si is retained in Narragansett Bay salt marshes, we summed the average spring and summer net Si flux (BSi and DSi) values (Table 3) to estimate that 20.8 kmol Si d^{-1} km^{-2} is imported into our study site over the entire growing season. Scaling this value up to the area of salt marshes in Narragansett Bay (13.7 km^2; Wigand and Roman 2012), we estimate that salt marshes retain 5.1 $\times$ 10^4 kmol Si in the estuary throughout the spring and summer seasons (180 d). Using the average spring and summer river Si (both DSi and BSi) flux from four nearby rivers in Massachusetts in 2011 (186 mol Si d^{-1} km^{-2}; Carey and Fulweiler 2013*b*) in combination with the draining area of Narragansett Bay (4690 km^2; Bricker-Urso et al. 1989), we estimate that salt marshes retain just over 30% of the Si imported into the Bay throughout the spring and summer periods.

The salt marshes of Narragansett Bay are representative of many organic-rich, sediment-starved marshes found throughout the northeastern United States, formed over the course of the last several thousand years, with vegetation zonation patterns typical of the region (Bricker-Urso et al. 1989; Wigand and Roman 2012).

Future research should continue to explore the ecological significance of marsh–estuarine Si exchange in marshes of different ages, with different sediment and vegetation types, and in systems dominated by nondiatom production, such as macroalgae or submerged aquatic vegetation. In addition, the contribution of benthic vs. pelagic diatoms to net Si fluxes also deserves attention.

Most marsh Si flux studies have highlighted the importance of DSi export from marshes, which supplies DSi necessary for diatom production. Our results presented here agree with this finding and highlight that DSi export from northeastern U.S. tidal marshes is important, especially during the spring when riverine DSi fluxes are at a minimum. However, the opposite service of Si import and retention by these marshes is also critical; we argue that the potential for salt marshes to increase the residence time of bioavailable Si within northeastern estuaries is an overlooked ecosystem service provided by these habitats. In the absence of these salt marshes, we hypothesize that Si availability in the estuary would decrease, with direct repercussions to phytoplankton species composition and carbon cycling. Like many other estuaries, over half of the marshes in Narragansett Bay have been lost in the last two centuries (Bromberg and Bertness 2005). As such, we wonder how this large-scale loss of salt marshes in the past has altered Si cycling at the land–sea interface. The role of tidal wetlands in linking terrestrial and aquatic Si cycling should not be overlooked as humans continue to modify coastal landscapes.

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