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Hydrologic forcing of submarine groundwater discharge: Insight from a seasonal study of radium isotopes in a groundwater-dominated salt marsh estuary

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Abstract

A seasonal study of radium-derived submarine groundwater discharge (SGD) and associated nitrogen fluxes was carried out in a salt marsh estuary between 2001 and 2003 (Pamet River Estuary, Massachusetts). Twelve-hour time series of salinity and radium at the estuary inlet were used to determine the relative importance of fresh versus saline SGD, respectively. The distinct radium ($^{228}Ra : ^{226}Ra$) isotopic signature of marsh peat pore water and aquifer-derived brackish groundwater was used to further partition the Ra-derived SGD estimate. Of these three groundwater sources, only the marsh-derived groundwater was constant across time. The ratio of brackish to fresh SGD was inversely correlated with water table elevation in the aquifer, suggesting that Ra-derived SGD was enhanced during dry periods. The various SGD fluxes were responsible for an average annual dissolved inorganic nitrogen (DIN) input of between 1.7 mol m^{-2} yr^{-1} and 7.1 mol m^{-2} yr^{-1} and a soluble reactive phosphate (SRP) flux of 0.13–0.54 mol m^{-2} yr^{-1}. Approximately 30% of the SGD-derived DIN and SRP flux is exported to coastal waters (Cape Cod Bay), whereas 70% is retained by the salt marsh ecosystem.

1 Submarine groundwater discharge (SGD) has been increasingly recognized as an important source of nutrients for a wide variety of coastal marine environments (Johannes 1980; Valiela et al. 1990; Krest et al. 2000). In some settings, subsurface input of nutrients has been shown to be more important than surface inputs, including both rivers and atmospheric deposition (Valiela et al. 1992). One major limitation in quantifying SGD-derived fluxes has been reliable techniques for determining the flux. Chemical tracers have become a popular tool for the study of SGD (e.g., Cable et al. 1996; Moore 1996). A primary desirable characteristic of chemical tracers of SGD is that they have a unique or dominant source in groundwater and are not present in any significant quantity in other vectors (e.g., river water or rainfall) for water flux to the coastal ocean.

Radium (Ra) isotopes have proven to be useful tracers of total SGD in many environments on both small and large scales, from salt marshes (Rama and Moore 1996; Krest et al. 2000; Charette et al. 2003) to estuaries (Charette et al. 2001; Kelly and Moran 2002; Yang et al. 2002) and to the continental shelf (Moore 1996). The chemical behavior of radium is such that its K_d decreases significantly in saline 2
environments, mainly because of cation exchange processes (Li and Chan 1979). Thus, radium is usually only enriched (relative to surface water) in brackish to saline groundwater; fresh SGD that does not interact with saline groundwater in ''subterranean estuary'' will not acquire a radium signal and hence may not be quantified (Mulligan and Charette 2006). This characteristic of the Ra-derived SGD tracer has led to some controversy and confusion in the literature, usually because of the observation that Darcy's Law and other traditional hydrogeologic-based groundwater flux estimates are often significantly lower than Ra-based SGD (Burnett et al. 2001; Smith and Zawadzki 2003). Such differences can often be attributed to the tendency for SGD to include a substantial component of seawater that has been recirculated through coastal marine sediments (Burnett et al. 2006).

The existence of four naturally occurring radium isotopes (^{224}Ra, $t_{1/2}$ = 3.66 days; ^{223}Ra, $t_{1/2}$ = 11.4 days; ^{228}Ra, $t_{1/2}$ = 5.75 years; ^{226}Ra, $t_{1/2}$ = 1,600 years) makes Ra particularly useful for quantifying multiple sources of SGD, such as fluid originating from confined versus surficial aquifers (Crotwell and Moore 2003; Moore 2003; Charette and Buesseler 2004). This approach is made possible through two primary mechanisms. First, aquifers with different principal mineral or sediment types can have differing degrees of uranium ($^{238}U \rightarrow {}^{226}Ra$; $^{235}U \rightarrow {}^{223}Ra$) and thorium ($^{232}Th \rightarrow {}^{228}Ra \rightarrow {}^{224}Ra$) series isotopes. Second, the frequency of seawater circulation through an aquifer can leave sediments, which are the ultimate source of Ra isotopes in groundwater, enriched in the shorter-lived isotopes and depleted in the longer-lived isotopes because of the relative differences in ingrowth rates from the thorium parents.

Here, I examine Ra-derived SGD and associated nitrogen fluxes in a salt marsh estuary (Pamet River Estuary, Massachusetts). This site was chosen because

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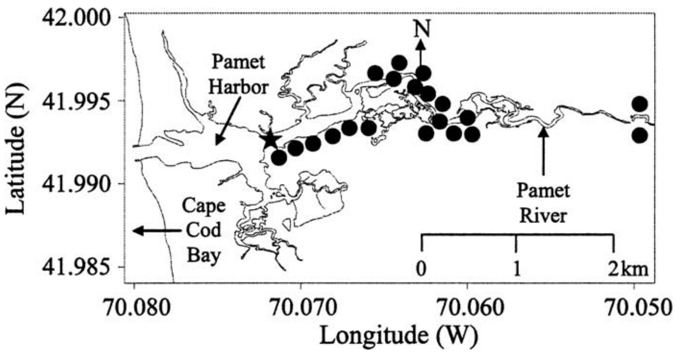

Fig. 1. Map of the Pamet River Estuary with the location of the time-series sampling indicated by a star and the location of the groundwater stations highlighted with solid circles; some groundwater stations were visited more than once during the two-year study period.

groundwater is the only source of freshwater to the system. By performing both salinity and radium mass balances during five time periods during the course of ~20 months, I determined the relative importance of fresh versus saline SGD, respectively. Also, I used the distinct radium (^{228}Ra : ^{226}Ra) isotopic signature of marsh peat pore water and aquifer-derived saline groundwater to estimate SGD fluxes for each of these sources using a three endmember mixing model. The results presented here suggest that radium isotopes will be useful for determining the dominant form of SGD-derived nitrogen in salt marsh estuaries (i.e., new vs. recycled nitrogen).

Study area

The Pamet River Estuary is located on outer Cape Cod in Truro, Massachusetts (Fig. 1). It has an area of 930,000 m^2 and a fairly large tidal range of >3 m, which means that it is very well flushed during each tidal cycle. Salinity in the surface waters range from 0 to 32. The freshwater endmember is almost exclusively derived from groundwater; the sediments of Cape Cod are highly permeable, therefore surface-water runoff is almost nonexistent except in the case of large rainfall events. The high salinity endmember is that of Cape Cod Bay, the body of water that exchanges with the Pamet during each tidal cycle. There are two groundwater lenses that supply the Pamet with freshwater, the Pamet Lens to the north and the Chequesset Lens to the south (Eichner et al. 1997). The hydraulic conductivity of the sediments is high and the hydraulic gradient of the water table elevations adjacent to the marsh are steep. These factors lead to a significant groundwater influence for this marsh system.

Methods

To investigate the dynamics of submarine groundwater discharge in salt marsh systems, a two-year seasonal study of Ra isotopes in the Pamet River Estuary, Truro, MA was undertaken. The study design involved a two-pronged approach. First, during each period (July 2001, March 2002, July 2002, November 2002, and March 2003), a 12-hour time-series sampling of Ra isotopes and nutrients was conducted at the inlet to the estuary (Fig. 1). For radium isotopic analysis, each hour 100 liters of water was filtered into a polyethylene barrel, which was then slowly pumped (~1 L min^{-1}) through magnesium dioxide (MnO_2)-coated acrylic fiber to extract the Ra (Moore and Reid 1976). Subsamples for nutrients and salinity were also collected at this time. Tidal height, temperature, and salinity were monitored every 15 min using a YSI 600XLM CTD. By using this sampling approach, a whole-marsh estimate of Ra export and hence SGD was obtained simply by knowing the net Ra flux (ebb tide minus flood tide inventories) and the tidal prism (630,000 m^3). Sample collection was always conducted on the highest spring tide of the month to maintain consistency between sampling periods.

More than 40 groundwater and pore-water samples were collected from various locations along the marsh edge and from within various sediment types (marsh peat, quartz sand) of the system. A drive-point piezometer system called Retract-A-Tip (AMS) was used to accomplish this task (Charette and Allen 2006). Briefly, the stainless steel piezometer was driven to the depth of interest. Samples were pumped through Teflon tubing using a peristaltic pump. For Ra analysis, groundwater was pumped directly through the fiber, and the filtrate (10–20 liters) was collected to determine the sample volume. Samples for nutrients were collected into 30-mL, acid-cleaned scintillation vials using a plastic syringe and Millipore Sterivex filter. Basic water properties, including salinity, pH, dissolved oxygen, and redox potential, were recorded using a YSI 600R and 650MDS handheld computer. The majority of the groundwater samples were collected during July 2002, although a number of samples were collected during the winter (March) and fall (November) time periods as well.

For the sediment desorption experiment, aquifer sands were collected from two locations: (1) from the inland portion of the aquifer such that the sediments had not been subject to saltwater intrusion and (2) from the marine portion of the aquifer, where they had been exposed to fully saline groundwater (~28–30) for an extended period of time (~decades). Groundwater was then collected from each location and passed through a column of MnO_2 fiber to remove the radium. The Ra-free water was filtered and mixed such that there were five treatments for each sediment type (salinity = 0, 7.5, 15, 22.5, 30). Each treatment was run in triplicate and consisted of a ~400-g aliquot of sediment added to 20 liters of Ra-free groundwater. After 48 hours, the water was filtered, and the desorbed Ra was concentrated onto MnO_2 fiber for analysis by the techniques described below.

Back in the laboratory, the MnO_2 fiber was rinsed and partially dried. Activities of ^{223}Ra ($t_{1/2}$ = 11.4 days) and ^{224}Ra ($t_{1/2}$ = 3.66 days) were measured on a delayed coincidence counter as described by Moore and Arnold (1996). The fiber was then ashed in a muffle furnace (820°C for 16 h), ground, and homogenized before being packed in a counting vial and sealed with epoxy to prevent ^{222}Rn loss (Charette et al. 2001). Once ^{222}Rn had reached secular equilibrium with its parent, activities of ^{226}Ra ($t_{1/2}$ = 1,600 yr) and ^{228}Ra ($t_{1/2}$ = 5.75 yr) were determined by γ-counting in a well detector (Canberra, model GCW4023) by the ingrowth of ^{214}Pb (352 keV) and ^{228}Ac (911 keV). Calibration of the well detector was achieved by counting four ashed MnO_2 fiber standards having the same activity range and geometry of the samples. Nutrient analyses (nitrate, phosphate, ammonium, and silicate) were performed using standard methods on a Lachat QuickChem 8000 flow injection analyzer.

Results

Radium isotope activities from the five time-series samplings are presented in Web Appendix 1 (http://
3 www.aslo.org/lo/toc/vol_xx/issue_x/xxxxal.pdf). For all time periods, there was an inverse correlation between tidal stage and radium activity (Fig. 2). In general, the flood tide (derived from Cape Cod Bay) radium values were consistently low, within the range of samples collected in other shelf regions (e.g., Moore 2000). However, there was significant variability in Ra activity between time periods for the ebb tide samples. For example, ^{226}Ra in March 2002 peaked at 62 dpm 100 L^{-1} compared with only 20 dpm 100 L^{-1} during March 2003.

For each individual time period, radium in surface water was generally constant above a salinity of ~25, then generally increased with decreasing salinity (Fig. 3). However, interestingly, radium isotopes did not display a consistent trend with salinity when compared between time periods. The ^{226}Ra maximum for March 2002 occurred at a salinity of ~27, whereas the highest ^{226}Ra for other periods was found at lower salinities (e.g., ~11 for March 2003). These differences were not correlated with the time of year (e.g., winter vs. summer), as had been observed for several earlier studies (e.g., Bollinger and Moore 1993; Kelly and Moran 2002).

The same temporal pattern in Ra isotopes was observed during the time-series sampling regardless of the time of year (Fig. 4). During flood tide, salinity was high and Ra was low; both values are typical for the source of this water, Cape Cod Bay. During early ebb tide, values were very similar to the Cape Cod Bay water. Then, approximately 3–4 hours after peak high tide, salinity began to drop and Ra increased. Looking in closer detail, during peak ebb tide, salinity began to increase whereas Ra dropped only slightly. The salinity minimum is derived from freshwater that has accumulated in the main channel of the estuary during the previous 12 hours. In the meantime, the low permeability salt marsh sediments continue to drain the high salinity water that occupied their pore spaces during the previous flood tide. The intermediate-salinity, high-Ra water is derived from this tidal pumping/inundation process.

The temporal pattern and trend with salinity in the time-series nutrients was very similar to that of radium, indicating that they both have a common source in groundwater (Web Appendix 1, Fig. 5). During March 2002, dissolved inorganic nitrogen (DIN) tracked the increase in radium during the outgoing tide (Fig. 4). Nutrient concentrations in

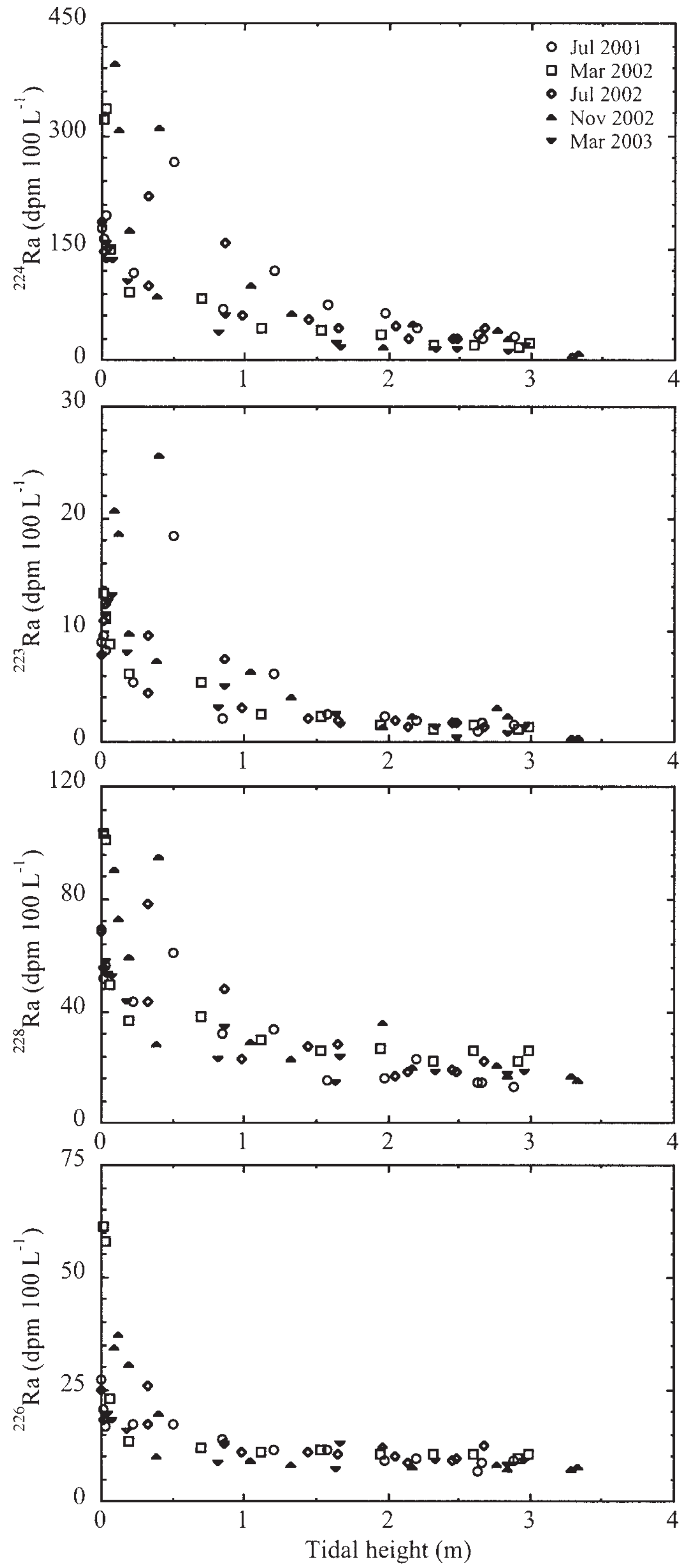

Fig. 2. Radium isotopes versus tidal height for the time-series surface-water samples.

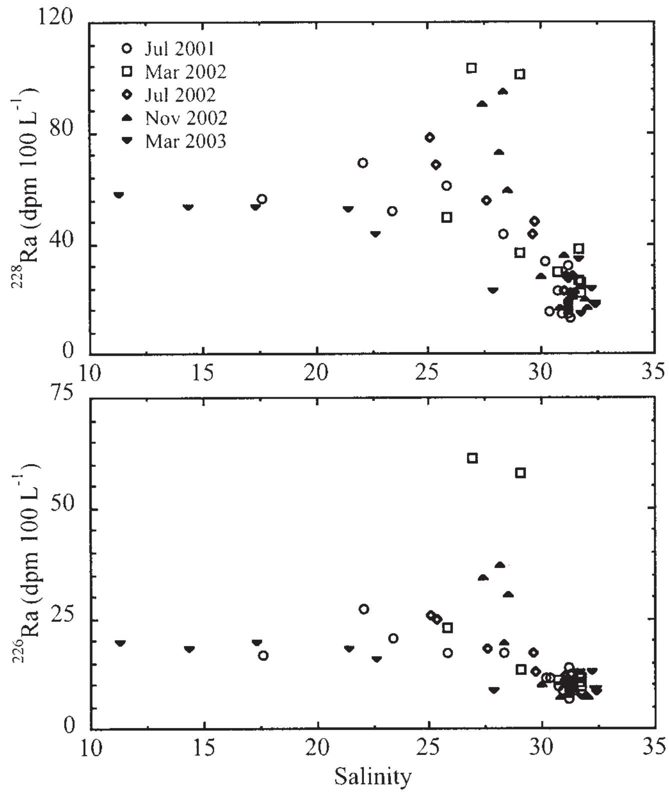

Fig. 3. Radium isotopes versus salinity for the time-series surface-water samples.

the water exiting the marsh were significantly higher than the flood tide water, a result of significant nutrient input combined with rapid estuarine flushing.

There was no discernable trend between groundwater salinity and radium or nutrients (Web Appendix 2, http:// www.aslo.org/lo/toc/vol_xx/issue_x/xxxxa2.pdf). This is likely a function of the fact that numerous kinds of pore-water samples were collected (groundwater seeps, marsh sediments, coarse-grained aquifer sediments) and that they were collected across wide spatial scales. For example, ^{226}Ra ranged from 2 dpm 100 L^{-1} (below average bay water) to 181 dpm 100 L^{-1} (~10× average estuarine surface water). On average, however, radium isotopes and nutrients were 2–3× enriched in groundwater relative to surface water.

Discussion

On an aerial basis, salt marshes are among the most productive ecosystems on earth (Schlesinger 1991). They play host to a wide range of plant and wildlife species and are hatcheries for many commercially important finfish. Many salt marshes were created as a result of glacial processes during the ice ages, and they are characterized as an accumulation of fine-grained sediment over the top of coastal plain or glacial outwash sediments. This creates a unique hydrogeologic environment, which for an ideal case is illustrated in Fig. 6.

In a coastal salt marsh, groundwater typically enters surface water via two pathways (Fig. 6). The shallow flow path is groundwater that passes from the unconfined aquifer through the marsh peat. This source also includes tidally pumped water that inundates these marsh sediments during each flood tide; as a result, the salinity of this groundwater is often indistinguishable from surface water and can even be hypersaline because of use of the freshwater by marsh plants. The intermediate flow path involves groundwater flowing beneath the marsh peat, where a deposit of silt and clay acts as a confining layer. This confining layer is often breeched by the permeable sediments of tidal creeks, which allows the groundwater to escape into the surface-water system. Such a breech is present in the main channel of the Pamet River system; this groundwater is usually brackish.

Analysis of groundwater samples collected along the estuary edge revealed that these two groundwater sources had distinct Ra isotopic (^{228}Ra : ^{226}Ra) signatures (Fig. 7a). The marsh groundwater endmember had high ^{228}Ra relative to ^{226}Ra (activity ratio of ~10–15) whereas the aquifer-derived groundwater had relatively low activity ratios (1–2). The explanation for this is related to two factors: (1) the frequency with which seawater circulates

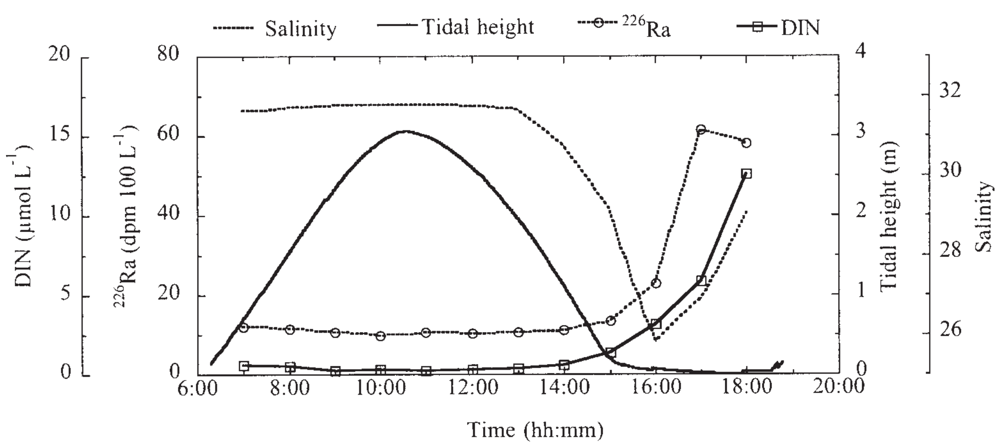

Fig. 4. Time series of ^{226}Ra, salinity, dissolved inorganic nitrogen, and tidal height at the Pamet River inlet during 28 March 2002. The same pattern was typically observed during all time periods, with only the order of magnitude of the ^{226}Ra activities changing.

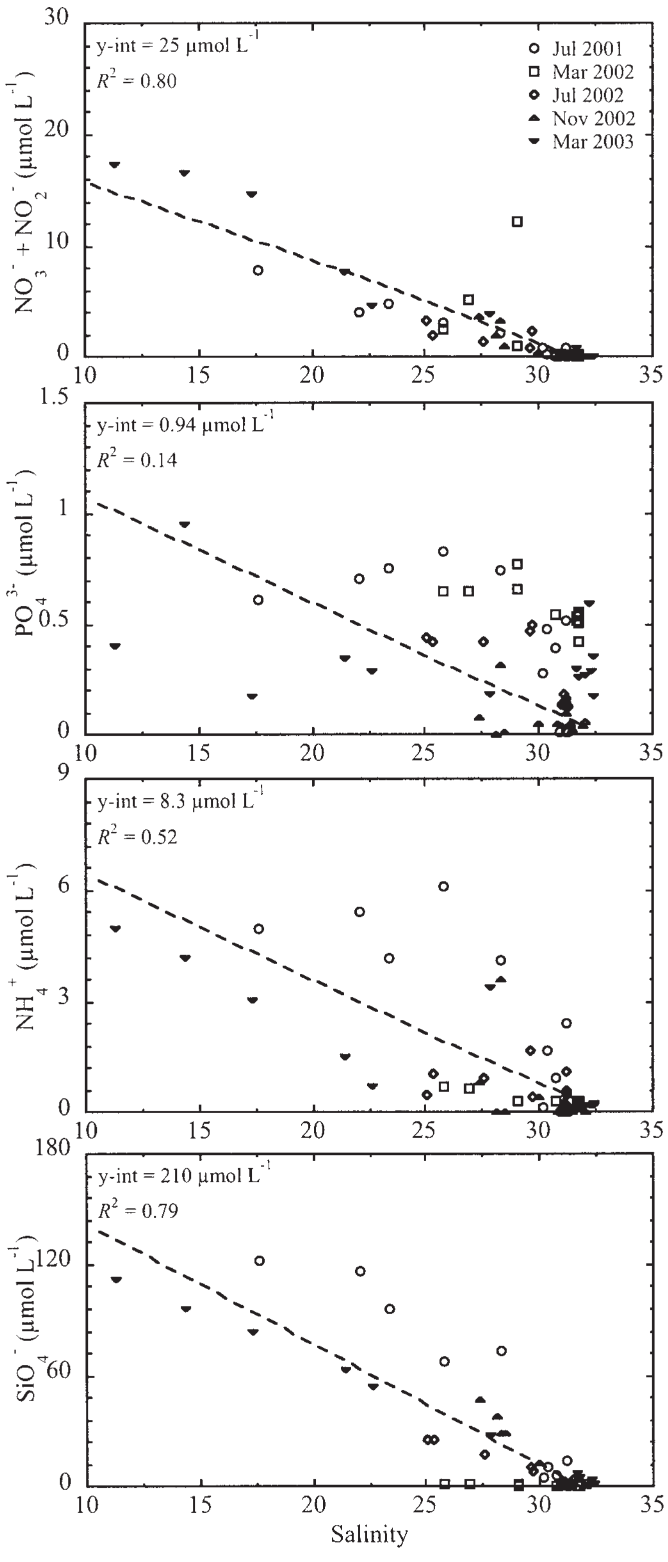

Fig. 5. Nutrients versus salinity for all time-series data. The curve fit includes all data.

through the sediment and (2) the regeneration rate of the particular radium isotope from its parent thorium isotope. Therefore, because the marsh sediments are repeatedly flooded on tidal time scales and because ^{228}Ra has a significantly shorter half-life than ^{226}Ra, marsh sediment-derived groundwater has unusually high ^{228}Ra : ^{226}Ra activity ratios (Rama and Moore 1996; Krest et al. 2000; Charette and Buesseler 2004).

These two distinct groundwater activity ratios enable us to construct a three endmember mixing model for data obtained during our time-series sampling at the inlet. In this model, the three sources of Ra to the estuary are marsh groundwater, brackish aquifer-derived groundwater, and coastal ocean seawater introduced to the Pamet from Cape Cod Bay during tidal mixing (Fig. 7b). The following three equations containing three unknowns (f_{co}, f_{marsh}, $f_{brackish}$) are linear and can therefore be solved by substitution.

$$f_{co} + f_{marsh} + f_{brackish} = 1 \quad (1)$$

$$^{228}Ra_{co} \times f_{co} + {}^{228}Ra_{marsh} \times f_{marsh} + {}^{228}Ra_{brackish} \times f_{brackish} = {}^{228}Ra_{surf} \quad (2)$$

$$^{226}Ra_{co} \times f_{co} + {}^{226}Ra_{marsh} \times f_{marsh} + {}^{226}Ra_{brackish} \times f_{brackish} = {}^{226}Ra_{surf} \quad (3)$$

The terms f_{co}, f_{marsh}, and $f_{brackish}$ are the fractions of water derived from the coastal ocean, marsh groundwater, and surficial aquifer, respectively, in a given sample. The endmember Ra activities are indicated by the subscripts, and $^{228}Ra_{surf}$ and $^{226}Ra_{surf}$ are the activities in the surface-water (surf) sample of interest. The endmember activities used were as follows (all units are dpm 100 L^{-1}): $^{228}Ra_{marsh}$ = 516 and $^{226}Ra_{marsh}$ = 36, $^{228}Ra_{brackish}$ = 180 and $^{226}Ra_{brackish}$ = 180 (Web Appendixes 1 and 2; Fig. 7). The coastal ocean endmember was based on the minimum value observed during flood tide for a given period (typically: $^{228}Ra_{co}$ = 15 and $^{226}Ra_{co}$ = 8). The brackish surficial aquifer Ra endmember was chosen as the sample with both the highest ^{226}Ra activity and lowest ^{228}Ra : ^{226}Ra AR (1.0). 5

There are several key assumptions associated with this approach. First and foremost, I assume that the two groundwater endmember ratios and Ra activities are relatively constant year round. By using the upper limit activities for each endmember, the model will provide a conservative lower limit estimate of the SGD flux. As for the estimate of the relative proportion of marsh versus brackish SGD, the two endmember ratios are so distinct that the model is relatively insensitive to small changes in ^{228}Ra : ^{226}Ra. In the following discussion, I also assume that (1) the marsh exchanges completely with the bay during each tidal cycle and (2) the tidal prism is well mixed. The former assumption is well founded given that the marsh is almost completely drained with the ebb tide, and the along-shore currents in the bay are relatively swift. The latter assumption is supported by the strong vertical and horizontal mixing that takes place when the marsh must drain through a narrow (~30 m) artificially constructed inlet.

The model was run for each data point collected during each of the 12-h inlet time-series sampling periods (Web

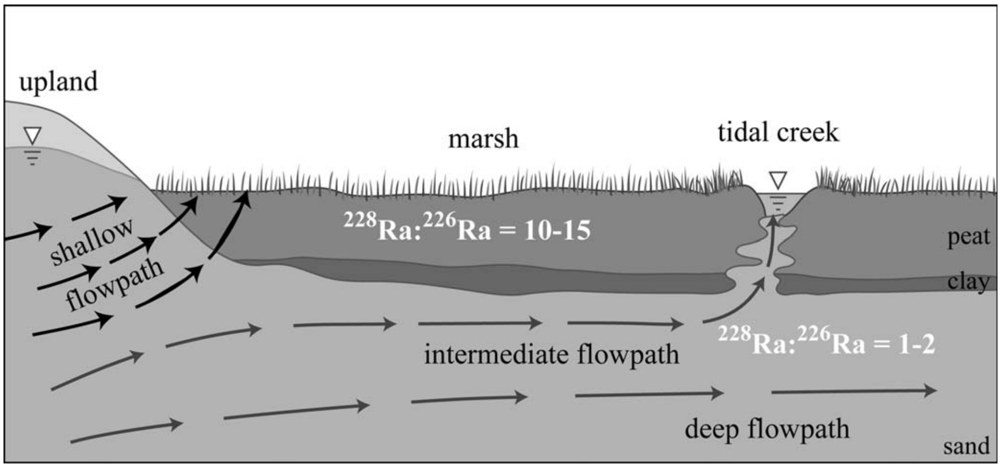

Fig. 6. Hydrogeology of a salt marsh ecosystem (adapted from Howes et al. 1996) with typical ^{228}Ra : ^{226}Ra activity ratios for the two groundwater endmembers.

Appendix 3, http://www.aslo.org/lo/toc/vol_xx/issue_x/
6 xxxxa3.pdf). As an example, in Fig. 8, I show the results for March 2002 only. During flood tide and the first few hours of the following ebb tide, nearly 100% of the Ra can be accounted for having originated from Cape Cod Bay. During the latter portion of the ebb tide, both the brackish and marsh contributions begin to increase. The marsh groundwater contribution to the Ra inventory peaks at 10%, whereas the brackish groundwater contribution tops out at 30%. Except for variation in the magnitude of the Ra contributions, this pattern was similar for all time periods.

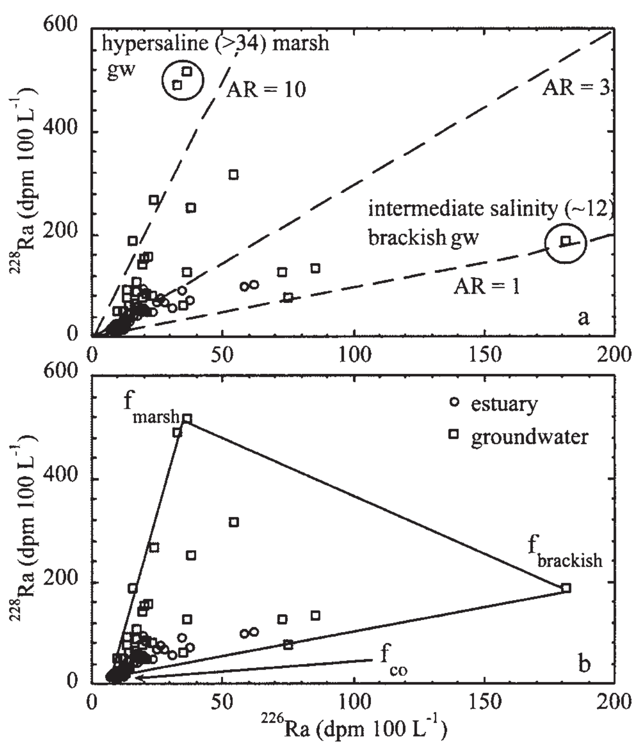

Fig. 7. ^{228}Ra versus ^{226}Ra for all groundwater (gw) samples, with activity ratios indicated by the dashed line (a), and groundwater and surface water with three endmembers used in the mixing model (b).

For each time period, I estimated the net fraction of each endmember discharging from the marsh by averaging the ebb tide f values (Web Appendix 3). I also estimated the percent fresh groundwater flux from the Pamet by conducting a simple salt balance for the ebb minus flood salinity values (which assumes all of the freshwater originated in the subsurface). Interestingly, whereas the brackish groundwater contribution varied by a factor of three for the five time periods, the marsh groundwater contribution was constant regardless of the season (Table 1). This result is not entirely unexpected and actually provides somewhat of an independent check on our mixing model; if dominated by tidal pumping of surface water, the amount of fluid that flows through the marsh pore waters should not vary with the season.

If the marsh groundwater contribution is relatively constant with time, then what factors explain the variability in the brackish, aquifer-derived groundwater contribution? To answer this question, I first converted the $f_{brackish}$ in Web Appendix 3 to a water flux estimate by multiplying by the tidal prism volume and 1.9 tides per day. It is important to note that the Ra-derived brackish SGD does include some (nonconstant) fraction of the salt-balance–derived fresh SGD. The results are shown in Fig. 9, which also shows the water table elevation from a U.S. Geological Survey monitoring well (USGS J561 MA-TSW) in the Pamet groundwater lens (north side of the marsh). Whereas fresh SGD correlates with water table elevation, the brackish groundwater flux showed the opposite trend: highest in March 2002 during the lowest aquifer water level of the 2-yr period, with the ratio of brackish plus marsh SGD to fresh SGD showing an inverse correlation (Fig. 10). I hypothesize that this relationship can be accounted for by an enhanced groundwater–seawater interaction in the shallow aquifer during this time.

My hypothesis can be explained as follows: water table height, a function of net recharge to the aquifer, will determine the location of the groundwater–seawater interface. During periods of net aquifer recharge, this

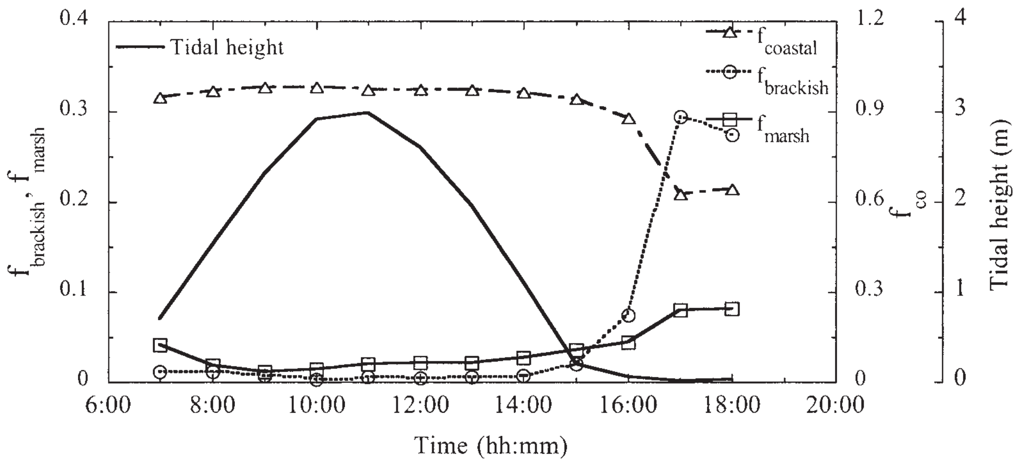

Fig. 8. Results from the three endmember mixing model for the inlet time-series samples collected during 28 March 2002.

interface will remain closer to the shoreline. Conversely, drought conditions (such as in March 2002) will result in a lowering of the water table and landward movement of the boundary. When the level of the water table drops, salt water intrudes deeper into sediments that have not been exposed to saline groundwater for a period of time and desorbs quantitatively more radium (and possibly nutrients like ammonium), which is subsequently delivered to the marsh via SGD. Periods of higher groundwater elevation were characterized by (relatively) lower brackish groundwater flux, a result of the brackish groundwater interacting with aquifer sediments that had already been exposed to seawater and therefore had been weathered of the majority of their surface-bound radium.

This hypothesis is supported by a simple desorption experiment, whereby sediment from the freshwater portion of the Cape Cod aquifer and sediment from the marine (saline groundwater) end were exposed to Ra-free seawater of varying salinity (Fig. 11). For all treatments (excluding freshwater), the aquifer sands that had never been exposed to saltwater intrusion yielded $\sim$25$\times$ more ^{226}Ra than the sediments that had been continually exposed to saline groundwater. In addition, the ^{228}Ra : ^{226}Ra activity ratio in the marine sands was significantly higher (3.2) than the freshwater sands (1.3, close to the parent isotope AR of $\sim$1), which demonstrates the effect of faster ^{228}Ra regeneration relative to that of ^{226}Ra in previously desorbed sediments.

The fresh SGD fluxes as estimated from the salinity balance for the Pamet River time-series data clearly do not correlate with the brackish or marsh SGD fluxes as predicted from the three endmember mixing model. If the source of the freshwater in the Pamet is indeed groundwater, then it must be freshwater that bypasses the fresh–saline groundwater mixing zone where the radium signal is typically imparted (Charette et al. 2003; Mulligan and Charette 2006). Radon, an inert noble gas, is enriched in groundwater of any salinity and therefore should be an ideal tracer of total SGD (fresh plus brackish plus marsh). Indeed, Allen and Charette (2004), in a multi-isotope tracer study of the Pamet River, reported that the radon-derived SGD value (1.5 m^3 m^{-2} d^{-1}) was balanced by the sum of the radium-derived SGD (0.77 m^3 m^{-2} d^{-1}) and the salinity balance (0.70 m^3 m^{-2} d^{-1}).

Past studies have stressed that SGD was a major source of nutrients to salt marshes (Valiela et al. 1978; Johannes 1980; Krest et al. 2000), and the Pamet River is no exception. During all time periods, nutrients displayed a significant inverse correlation with salinity, indicating a brackish or fresh groundwater endmember (Figs. 4 and 5). In addition, nitrate, ammonia, and phosphate concentrations were low near high tide and high near low tide (Web Appendix 1), suggesting input by SGD. Using the average groundwater nutrient concentrations compiled in Web Appendix 2 and the groundwater fluxes from Table 1, I can estimate nutrient fluxes to the marsh via SGD for

Table 1. Radium-derived submarine groundwater discharge rates for the Pamet River Estuary.

Sampling period	Tidal prism (10^6 m^3) [a]	Ebb tide average f_{marsh} [b]	$f_{brackish}$ [c]	f_{fresh} [d]	SGD_{marsh} [e] = [b] $\times$ [a]	$SGD_{brackish}$ (10^3 m^3 d^{-1}) [f] = [c] $\times$ [a]	SGD_{fresh} [g] = [d] $\times$ [a]
Jul 2001	0.63	0.04	0.05	0.14	43	58	168
Mar 2002	0.63	0.04	0.10	0.07	53	117	89
Jul 2002	0.63	0.04	0.03	0.05	42	30	65
Nov 2002	0.63	0.03	0.06	0.06	40	68	75
Mar 2003	0.63	0.03	0.03	0.27	40	40	328

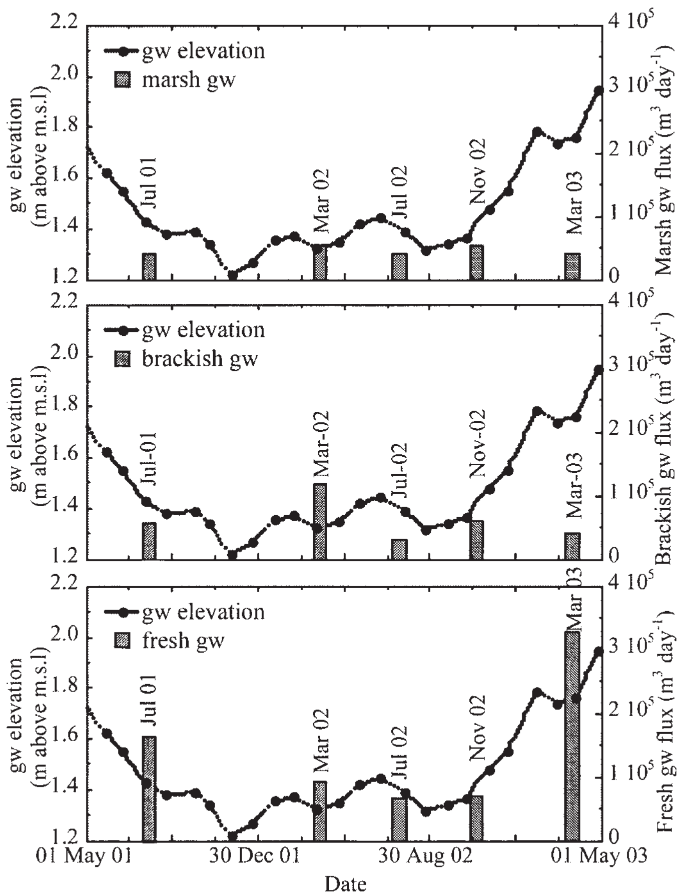

Fig. 9. Marsh, brackish, and fresh groundwater (gw) flux (cubic meters per day) to the Pamet River Estuary for five time periods between July 2001 and March 2003. Also shown is the groundwater elevation (meters above sea level) from a nearby U.S. Geological Survey monitoring well (J561 MA-TSW).

each time period. The results for DIN (nitrate plus ammonium) are summarized in Table 2. Given that the Ra approach alone may not capture all of the groundwater input to the system, two methods for SGD-derived DIN

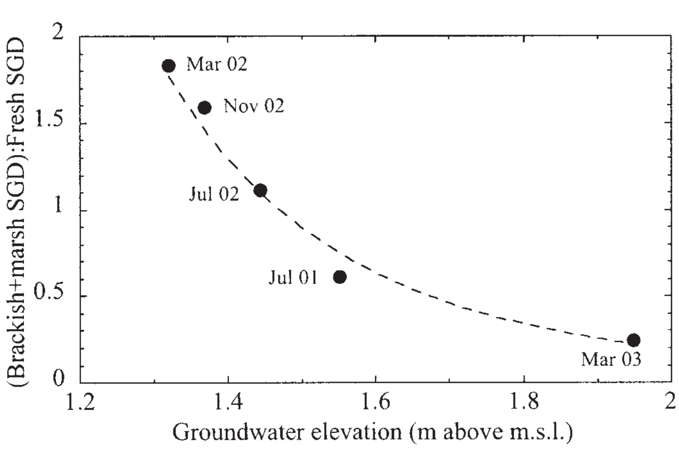

Fig. 10. Ratio of the Ra-derived SGD (brackish + marsh) to the salt-balance–derived SGD (fresh) versus water table elevation in a nearby U.S. Geological Survey monitoring well (J561 MA-TSW).

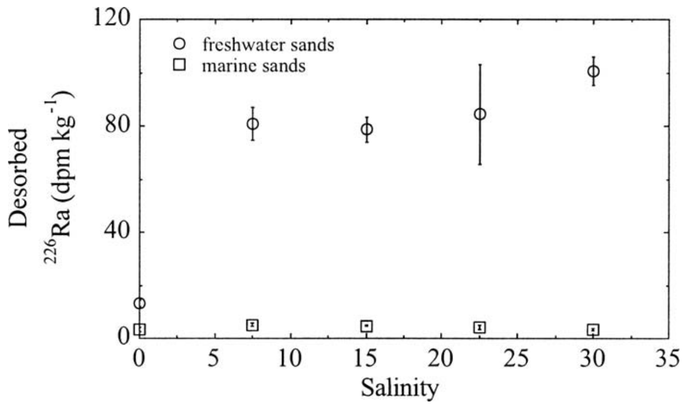

Fig. 11. ^{226}Ra activity released per kilogram of sediment as a function of salinity during the desorption experiment. The error bars represent the standard deviation of the triplicate measurements for each treatment.

input were used: (1) using the SGD_{fresh} estimate (based on the salt balance) and (2) using the sum of the SGD_{marsh} and $SGD_{brackish}$ (Ra-derived) estimates. In both cases, a single groundwater DIN average (41 μmol L^{-1}) was used, which may be an overestimate (for the marsh pore-water samples) given that the majority of the samples were collected during the summer, when respiration rates in the marsh sediments are in theory at a maximum. Also, there is clearly a great deal of variability in the groundwater DIN concentration, which cannot be easily translated into an uncertainty on the average used for the flux calculation given that the variability is likely real because of the various point (e.g., wastewater plumes) and nonpoint (e.g., organic carbon remineralization) nutrient sources. The only way to reduce uncertainty in such situations is to collect a large number of samples from along the entire length of the estuary at the point just before discharge, which has been done in this case. In any case, this approach should provide reasonable upper and lower limit estimates.

For the salt-balance method, DIN inputs ranged from $8.1–41 \times 10^3$ mol d^{-1} compared with $3.0–7.0 \times 10^3$ mol d^{-1} for the Ra-derived SGD estimate. Using a marsh area of 9.3×10^5 m^2, these fluxes correspond to an average annual DIN input of between 1.7 mol m^{-2} yr^{-1} and 7.1 mol m^{-2} yr^{-1}. Given the average groundwater soluble reactive phosphate (SRP) of 3.1 μmol L^{-1}, the corresponding SRP input to the Pamet River ranges from 0.13 mol m^{-2} yr^{-1} to 0.54 mol m^{-2} yr^{-1}. These values are in the upper range of SGD-derived DIN and SRP fluxes to coastal embayments as compiled by Hwang et al. (2005).

Are these inputs balanced by nutrient export from the marsh? For all time periods, nutrient concentrations peak during ebb tide, indicating a net source from the marsh to coastal waters (e.g., DIN in Fig. 4). However, despite the relatively high surface-water nutrient concentrations in this estuary, except in the case of silicate, extrapolating the channel time-series data to a salinity of zero (Fig. 5) yields values less than the groundwater averages (Web Appendix 2), which suggests nutrient uptake by the marsh ecosystem.

To calculate nutrient export from the marsh, I used the average ebb tide minus the average flood tide concentration

Table 2. DIN fluxes in the Pamet River Estuary.

Sampling period	DIN input (method)		DIN output (10^3 mol d^{-1})	Output-input (method)	
	(SGD_{fresh})	(SGD_{marsh} + $SGD_{brackish}$)		(SGD_{fresh})	(SGD_{marsh} + $SGD_{brackish}$)
Jul 2001	21	4.2	6.5	15	−2.3
Mar 2002	12	7.0	4.2	7.5	2.8
Jul 2002	8.1	3.0	1.8	6.3	1.2
Nov 2002	8.9	4.6	1.7	7.1	2.9
Mar 2003	41	3.3	11	30	−7.9
average	18	4.4	5.1	13	−0.7
avg. (mol m^{-2} yr^{-1})*	7.1	1.7	2.0	5.1	

* Assuming marsh surface area = 9.3×10^5 m^2

and multiplied the excess by the tidal prism volume (6.3×10^5 m^3). For DIN, these output fluxes, which range from 1.7–11 $\times$ 10^3 mol d^{-1}, are reported in Table 2. In all cases, except during times of extreme freshwater input (July 2001 and March 2003), DIN output exceeds input from SGD. Assuming that nutrient uptake by the marsh is occurring during all time periods, the two exceptions suggest that the Ra-approach does not capture total groundwater flow and associated nutrients during these extreme events.

Using the average annual outputs minus inputs for this system (SGD_{fresh} estimate), I estimate a net salt marsh DIN uptake of 5.1 mol m^{-2} yr^{-1} (0.38 mol m^{-2} yr^{-1} for SRP). This DIN balance implies that approximately 30% of the SGD-derived DIN flux is exported to coastal waters (Cape Cod Bay) whereas 70% is retained by the salt marsh ecosystem (SRP balanced in exactly the same way: 30/70%). For the Nauset Marsh system, which is very similar to the Pamet and is located only 20 km to the south, Roman et al. estimated that 72% of the total productivity was attributed to the marsh grass *Spartina*. Using a carbon : nitrogen ratio of 25 for this species (Valiela and Teal 1974 as cited in Gallagher 1975), I estimate a net salt marsh primary productivity of 130 mol C m^{-2} yr^{-1}. This compares quite favorably with the estimate of Roman et al. (1990) for the nearby Nauset Marsh (160 mol C m^{-2} yr^{-1}). It is important to note that the roles of dissolved and particulate organic nitrogen were not considered in these budget calculations. In the case of the productivity estimate, I also did not account for denitrification as a potential alternative DIN sink. In either situation, however, the marsh was clearly a net source of DIN to coastal waters.

The implications of these results are several-fold. First, the Ra-derived SGD approach may not capture all of the fresh groundwater input to the coastal zone. Despite this fact, numerous studies have shown that they are excellent predictors of groundwater nutrient flux to the coastal zone (Krest et al. 2000; Charette et al. 2001; Moore et al, 2002). This is attributable to the fact that Ra accounts for the chemical transformations (e.g., denitrification, ammonium mobilization) that occur when fresh and salty groundwater interact before discharge into surface waters. Second, water table elevation likely plays a major role in the flux of groundwater-derived elements to coastal waters and perhaps in opposition to conventional wisdom (Michael et al., 2005; e.g., the wet season may not be associated with the peak flux in groundwater-derived chemicals). Last, radium isotopes are valuable tools for quantifying different groundwater sources in coastal regions. For example, this technique could be used to determine what fraction of nutrient inputs to an estuary is a recycled (e.g., marsh sediment pore water) versus a new source (e.g., aquifer-derived groundwater) to the system.

Numerous studies within the past several decades have reached the same conclusion: SGD plays a major role in the productivity of coastal ecosystems (e.g., Johannes 1980; Capone and Bautista 1985; Valiela et al. 1990). However, our understanding of SGD to coastal waters and its potential for carrying a significant nutrient burden is still far from complete (Slomp and van Cappellen 2004). Further studies shall concentrate on defining better the variability in space, time, and composition of SGD and the refinement of geochemical tracers and other techniques for quantifying the flux.

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