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Seasonal changes in groundwater input to a well-mixed estuary estimated using radium isotopes and implications for coastal nutrient budgets

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Abstract

^{226}Ra (half-life 1,600 yr) and ^{228}Ra (half-life 5.75 yr) were used as tracers to determine seasonal changes in groundwater input to the Pettaquamscutt estuary from June 1999 to June 2000. Ra isotopes were observed to be in excess of activities due to input from streams, Rhode Island Sound water, and particle desorption. The source of excess ^{226}Ra and ^{228}Ra within the estuary is attributed to groundwater transport of Ra derived from the weathering of bedrock within the Pettaquamscutt watershed. Short-lived ^{224}Ra (half-life 3.66 d) was used to calculate an average residence time of the estuary of 8 ± 4 d. Box models used to constrain seasonal changes in groundwater input to the estuary indicate highest groundwater input in the summer (6.4–20 L m^{-2} d^{-1}) and lowest values in the winter (2.1–6.9 L m^{-2} d^{-1}). These Ra-derived groundwater fluxes are similar to rates of aquifer recharge over the annual cycle. Using these Ra-derived groundwater fluxes, the input of inorganic nitrogen and phosphorus from groundwater to the Pettaquamscutt was estimated at 61–180 mmol m^{-2} yr^{-1} and 4.4–13 mmol m^{-2} yr^{-1}, respectively.

The discharge of groundwater to coastal waters represents an important source of dissolved nutrients and contaminants that may affect chemical and biological processes in coastal ecosystems (Johannes 1980; Valiela et al. 1990; Simmons 1992; Burnett et al. 2001). A primary difficulty associated with quantifying the input of submarine groundwater to the coastal marine environment is the diffuse and heterogeneous nature of groundwater flow. Seasonal changes in precipitation and evaporation may result in significant variations in groundwater flow over the annual cycle. Groundwater discharge has been determined using seep meters and hydraulic models (Freeze and Cherry 1979; De Meneses 1990; Nowicki et al. 1999; Burnett et al. 2002). Seep meters provide a discrete measure of groundwater input; however, they may not provide a reliable estimate of the large-scale diffuse flux (Freeze and Cherry 1979; Cable et al. 1997; Moore 1999; Nowicki et al. 1999; Burnett et al. 2002). Hydraulic models based on Darcy's Law used to calculate the diffuse flow produced by a hydraulic head require detailed characterization of the flow media (Freeze and Cherry 1979; De Meneses 1990).

The naturally occurring radionuclides ^{226}Ra (half-life 1,600 yr) and ^{228}Ra (half-life 5.75 yr), produced by alpha decay of ^{230}Th (half-life 7.54×10^{4} yr) and ^{232}Th (half-life 1.41×10^{10} yr) (Firestone 1996), respectively, are potentially useful tracers of groundwater input to coastal zones. Sources of Ra to an estuary include in situ production, riverine input, desorption from suspended particles, and groundwater input, whereas the removal of Ra from estuaries is typically dominated by tidal flushing (Li et al. 1977; Li and Chan 1979; Elsinger and Moore 1980; Fanning et al. 1981; Bollinger and Moore 1993; Hancock and Murray 1996; Moore 1996; Rama and Moore 1996; Moore 1997*a,b*; Scott 1998; Hussain et al. 1999; Krest et al. 1999, 2000; Charette et al. 2001; Scott and Moran 2001; Burnett et al. 2002). The application of Ra isotopes as tracers of groundwater input to coastal systems is based on balancing the input of ^{226}Ra from groundwater with the removal of excess ^{226}Ra due to tidal flushing. With this approach, several recent studies have indicated that groundwater input is spatially variable and represents a significant source of dissolved chemicals to coastal systems (Moore 1996; Rama and Moore 1996; Krest et al. 1999, 2000; Charette et al. 2001; Scott and Moran 2001); however, none of these studies have evaluated seasonal changes in groundwater input.

In this investigation, measurements of ^{226}Ra and ^{228}Ra in a well-mixed estuary, the Pettaquamscutt estuary, and a box model were used to estimate changes in groundwater input on a monthly basis from June 1999 to June 2000. In addition, $^{224}\mathrm{Ra}_{xs}/^{228}\mathrm{Ra}_{xs}$ activity ratios were used to constrain the residence time of Ra within the estuary. Finally, groundwater nutrient (N, P) measurements were combined with the Ra-derived groundwater fluxes to calculate the corresponding input of nitrogen and phosphorus to the Pettaquamscutt estuary.

Methods

Study area—The Pettaquamscutt estuary is located adjacent to Narragansett Bay in southern Rhode Island and discharges into Rhode Island Sound (Fig. 1). The estuary is 10 km in length and has an average depth of 2 m (Table 1). Glacial outwash sediments characterize the valley, while glacial till fringes the watershed (Hahn 1959; Johnson and Marks 1959; Lang 1961; Gaines 1975). The underlying bedrock is predominantly Rhode Island Formation metasedimentary rock, consisting of sandstone, conglomerate, schist, and graphite (Nevins 1991; Hermes et al. 1994). The northwest portion of the watershed is characterized by Esmond

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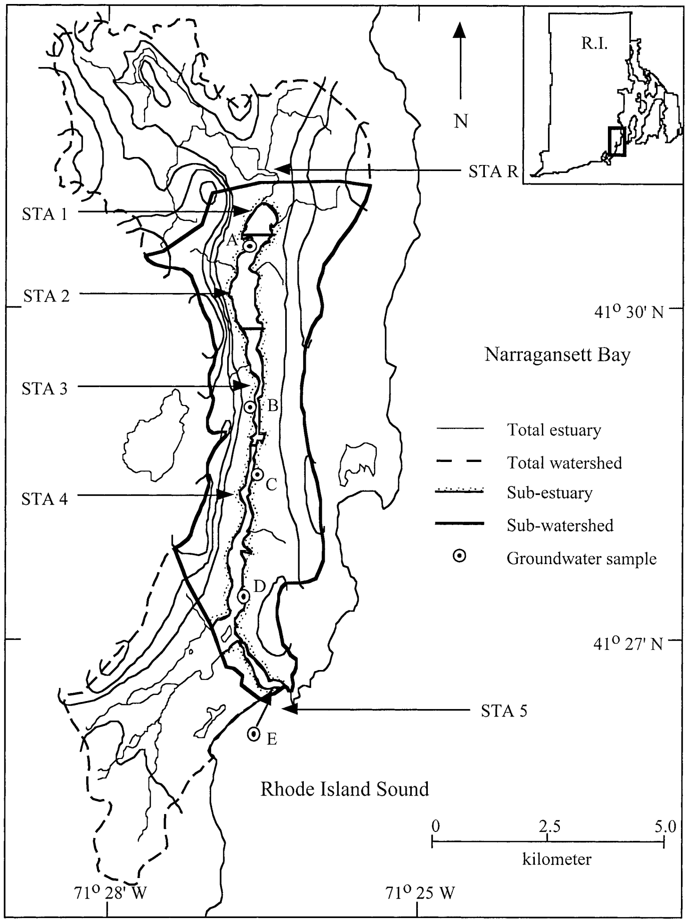

Fig. 1. Topographic map of the Pettaquamscutt estuary (15-m intervals). Arrows designate sample stations, lines indicate box boundaries. Pettaquamscutt Cove is located at the southern end of the estuary.

Plutonic granite gneiss and augen granite gneiss, while the southern extent is fringed by Narragansett Pier granite (Hermes et al. 1994). The southern end of the estuary has an extensive salt marsh, whereas the northern estuary is characterized by two deep (maximum depth: 20 m and 12 m), stratified, anoxic basins (Gaines 1975; Scranton et al. 1995). Gilbert Stuart Stream, located at the northern end, is the primary surface source of freshwater. Circulation is dominated by tidal mixing, with a spring tidal prism of 1×10^6 m^3 (Siffling 1997).

A hydrologic model of the Pettaquamscutt estuary indicates groundwater input to the Pettaquamscutt of up to $\sim 3 \times 10^7$ L d^{-1}, which is equivalent to approximately 60% of the freshwater input from Gilbert Stuart Stream (De Meneses 1990). De Meneses (1990) also reported spatial and seasonal variations in groundwater flow, and Siffling (1997) determined that the input of freshwater required to balance the tidal exchange was approximately 2×10^5 m^3 d^{-1}. The input of freshwater from Gilbert Stuart stream is $\sim 1 \times 10^5$ m^3 d^{-1} (Gaines 1975; De Meneses 1990; Siffling 1997), which suggests that only ~50% of the calculated freshwater transport may be attributed to input from Gilbert Stuart Stream, thereby implying a significant input from groundwater.

Table 1. Dimensions based on station distribution in the Pettaquamscutt River estuary and watershed area.

Station	Area ($\times 10^5$ m^2)	Depth (m)	Volume ($\times 10^5$ m^3)	Volume (%)
Sta. 1	2.3	3	6.9	18.7
Sta. 2	6.7	3	20.1	54.5
Sta. 3	1.9	1	1.9	5.1
Sta. 4	8.0	1	8.0	21.7
Total	18.9		36.9	100
Total watershed	355			
Effective watershed	145			

Sample collection and Ra analysis—Sample collection was conducted at five stations (Sta. 1–5) located along the salinity gradient of the Pettaquamscutt estuary on a monthly basis from June 1999 to June 2000 (Fig. 1). In all cases, samples were collected at high tide from the center of the estuary. Surface water samples (~100 liters) were collected for Ra isotopic analysis using 20-liter cubitainers. Groundwater samples were collected in August 2000 at four stations located in the salt marsh area of the southern end of the estuary and at one station in the upper pond area (Fig. 1). A 1.5-m steel tube (“marsh sipper”) was driven through the sediment at 10-cm depth intervals until water could be manually drawn using a 30-ml polyethylene syringe. Approximately 600 ml of water was collected for salinity, ^{226}Ra, and nutrient analysis.

Samples were filtered through a 1-μm polypropylene cartridge prefilter followed by two 5-μm MnO_2-impregnated cartridges connected in series (Mn*A* and Mn*B*). The flow rate was adjusted to <1 L min^{-1}. The collection efficiency (CE) of the cartridges was calculated using

$$\mathrm{CE} = 1 - \left(\frac{\mathrm{Mn}B}{\mathrm{Mn}A}\right) \qquad (1)$$

where Mn*A* and Mn*B* represent the counts per minute (cpm) of ^{226}Ra on the respective *A* and *B* MnO_2 cartridges. Collection efficiencies ranged from 80 to 90% at flow rates of <1 L min^{-1} for Ra (Kelly 2001). The MnO_2 cartridges were dried at 80°C for 24 h and then combusted in a muffle furnace at 500°C for 12 h. The cartridge ash was packed in polystyrene counting vials to a constant geometry (4 ml, 3.5 g) and capped with epoxy to prevent loss of ^{222}Rn (Scott 1998; Kelly 2001).

Samples were analyzed for ^{226}Ra, ^{228}Ra, and ^{224}Ra by gamma spectrometry using a Canberra pure germanium well detector, model GCW 3023 (active volume = 154 cm^3). Samples were stored for a period of at least 50 h after being capped with epoxy to allow ^{212}Pb (half-life 10.64 h) to reach secular equilibrium with ^{224}Ra and ^{228}Ac (half-life 6.15 h) to reach secular equilibrium with ^{228}Ra. The Mn*A* cartridges were analyzed at 238.6 keV and 911.6 keV for ^{212}Pb and ^{228}Ac, respectively (Moore 1984). Samples required a minimum of 14 d for ^{226}Ra to reach secular equilibrium with ^{214}Pb (half-life 26.8 m). The 351.9 keV peak was analyzed for ^{214}Pb on both the Mn*A* and Mn*B* cartridges (Moore 1984). The Mn*A* cartridges were counted to an uncertainty of

$<\pm 5\%$ error and the Mn*B* cartridges were counted to $<\pm 15\%$ (1 σ).

Particles were removed from groundwater samples by filtering through Whatman GF/F filters (0.7 μm nominal pore size) prior to Ra analysis. Each sample was analyzed three times for ^{226}Ra by ^{222}Rn emanation (Mathieu et al. 1988). Samples (~200 ml) were placed in ^{222}Rn extraction bottles and brought up to a volume of ~500 ml using 1.5 N HCl, then equilibrated for at least 14 d prior to analysis.

Ancillary methods—Temperature and salinity were determined on all surface and groundwater samples. Temperature was measured in situ using a thermometer. Salinity samples were collected in glass bottles and analyzed using a Guildline Autosal 8400 salinometer. Groundwater samples for analysis of dissolved nutrients (NH_4^+, NO_3^-, NO_2^-, and PO_4^{-3}) were collected in acid-washed high-density polyethylene bottles and filtered through Whatman GF/F filters. Samples were stored frozen until analysis using a Quickchem 8000 flow injection nutrient analyzer.

Results

Hydrography—The precipitation record for Kingston, Rhode Island, (10 km west of the Pettaquamscutt, www.ncdc.noaa.gov) indicates that most of the precipitation occurred toward the second half of the sampling period (Fig. 2A). Surface water temperature (volume-weighted average) from the Pettaquamscutt estuary and adjacent Rhode Island Sound exhibits significant seasonal variability (Fig. 2B). The warmest temperatures were observed in the summer of 1999 (~23–30°C), while the coolest temperatures were observed in the winter of 2000 (~2–5°C). The seasonal change in temperature in the estuary was larger than in Rhode Island Sound. The volume-weighted average salinity for the Pettaquamscutt decreased from June 1999 (~15–20‰) to June 2000 (~10–15‰), whereas the salinity of Rhode Island sound was relatively constant at ~31‰ (Fig. 2B). The observed decrease in the salinity of the estuary is consistent with the increase in precipitation over the study period.

Surface water Ra—Surface water Ra activities (dpm 100 L^{-1}) are listed in Table 2. Ra activities exhibit significant spatial and seasonal variability within the Pettaquamscutt estuary. Riverine (Sta. R) and Rhode Island Sound (Sta. 5) ^{226}Ra activities were uniform over the annual cycle, averaging 13.7 ± 0.3 dpm 100 L^{-1} and 14.6 ± 2.1 dpm 100 L^{-1}, respectively. Activities of ^{226}Ra within the estuary were consistently elevated relative to both low- and high-salinity end-member values, ranging from 12 to 50 dpm 100 L^{-1}. Riverine ^{228}Ra activities were not constant throughout the annual cycle, ranging from 13.8 to 79.5 dpm 100 L^{-1}. Activities of ^{228}Ra in Rhode Island Sound were nearly constant throughout the year, averaging 6.6 ± 1.5 dpm 100 L^{-1}. Within the estuary, ^{228}Ra activities were also consistently above low- and high-salinity end-member values, ranging from 6.4 to 49.5 dpm 100 L^{-1}. For ^{224}Ra, riverine and Rhode Island Sound activities ranged from 14.7 to 108 dpm 100 L^{-1} and 2.9 to 21.7 dpm 100 L^{-1}, respectively. Within the estuary, ^{224}Ra was enriched relative to the low- and high-salinity end members, ranging from 4.3 to 99.4 dpm 100 L^{-1}.

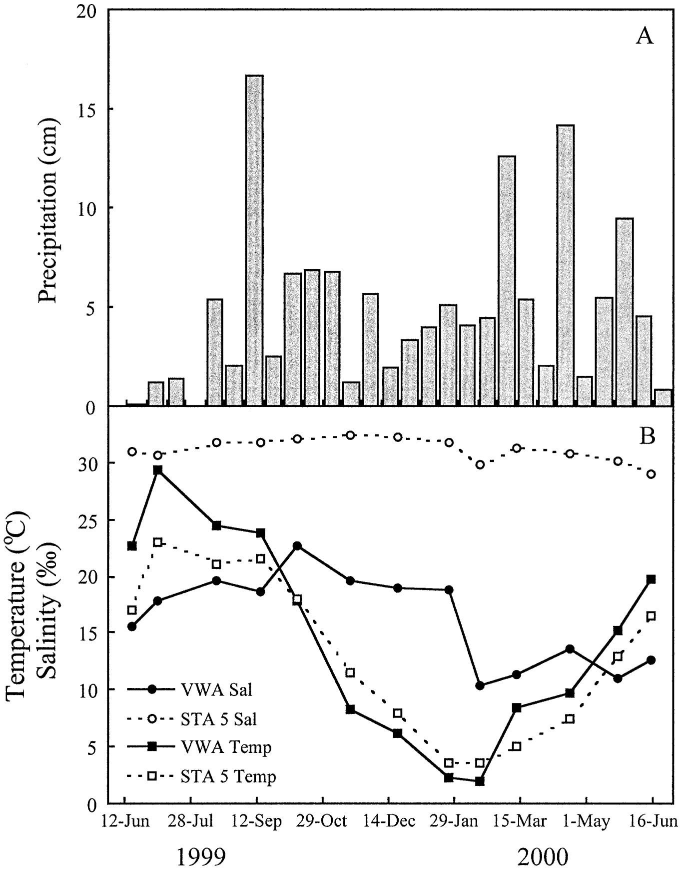

Fig. 2. Seasonal changes in (A) total precipitation and (B) volume-weighted average (VWA) surface water temperature and salinity within the Pettaquamscutt River watershed from 1 June 1999 through 30 June 2000 (www.ncdc.noaa.gov). Each precipitation column represents a 2-week total.

The study period can be divided into four seasons: summer (June 1999 through August 1999), fall (September 1999 through November 1999), winter (December 1999 through February 2000), and spring (March 2000 through June 2000). ^{226}Ra activities were highest in the summer (23.9–51.1 dpm 100 L^{-1}) and lowest in the winter (12.5–22.6 dpm 100 L^{-1}). Fall and spring values were of similar magnitude (17.6–50.5 dpm 100 L^{-1}). Also, summer ^{228}Ra values were highest (30.0–49.5 dpm 100 L^{-1}), winter activities were lowest (5.7–20.9 dpm 100 L^{-1}), and fall and spring values were intermediate (6.4–48.7 dpm 100 L^{-1}).

Activities of ^{226}Ra, ^{228}Ra, and ^{224}Ra observed in this study are comparable to those from other coastal studies. For example, Scott and Moran (2001) report ^{226}Ra values ranging from 16.5 to 76.9 dpm 100 L^{-1} for southern Rhode Island coastal salt ponds. Ra activities for Waquoit Bay (Cape Cod) have been reported to range from 4.3 to 18.4 dpm 100 L^{-1} for ^{226}Ra, 76.7 to 11.6 dpm 100 L^{-1} for ^{228}Ra, and 13.1 to 111 dpm 100 L^{-1} for ^{224}Ra (Charette et al. 2001). For the North Inlet Salt Marsh (South Carolina), Krest et al. (2000) report that ^{226}Ra ranged from 10 to 72 dpm 100 L^{-1}, and that ^{228}Ra ranged from 13 to 110 dpm 100 L^{-1}.

Table 2. Activities of ^{226}Ra, ^{228}Ra, and ^{224}Ra in the Pettaquamscutt River estuary collected monthly from June 1999 through June 2000. Units are in dpm 100 L^{-1}. NA designates a sample not analyzed. Ice designates frozen stations.

	1999						
	17 Jun	6 Jul	16 Aug	15 Sep	11 Oct	17 Nov	21 Dec
^{226}Ra							
Sta. R	13.53±1.01	14.04±1.23	NA	NA	NA	NA	NA
Sta. 1	39.22±3.86	37.15±3.97	23.87±3.06	43.56±5.70	25.45±6.76	27.43±4.79	12.51±1.81
Sta. 2	44.78±4.20	46.58±4.63	46.22±3.93	50.52±4.65	36.64±4.00	41.64±4.27	23.59±2.54
Sta. 3	43.97±3.49	47.09±4.74	47.14±3.77	35.40±3.32	33.98±3.84	33.52±3.91	21.31±2.32
Sta. 4	NA	43.02±3.59	51.05±3.61	29.33±2.04	25.42±2.02	32.73±2.72	25.83±1.85
Sta. 5	14.89±1.45	16.75±1.94	17.45±1.91	16.79±1.60	14.75±1.96	17.51±1.52	14.39±1.58
^{228}Ra							
Sta. R	54.95±5.71	79.49±9.41	NA	NA	NA	NA	NA
Sta. 1	38.18±3.57	49.52±5.62	44.53±5.90	9.30±1.27	7.86±2.07	8.70±1.53	10.84±1.61
Sta. 2	31.34±2.81	37.04±3.99	31.30±2.66	30.89±2.68	24.80±2.72	28.03±2.79	16.38±1.59
Sta. 3	30.61±2.36	41.43±4.39	29.99±2.59	25.29±2.32	26.02±2.82	26.76±3.16	18.08±1.86
Sta. 4	NA	37.59±3.21	37.16±2.84	23.37±1.57	16.52±1.35	29.87±2.34	8.43±1.10
Sta. 5	5.93±0.58	7.20±0.85	8.08±0.92	6.26±0.74	8.01±1.08	6.80±0.67	6.17±0.65
^{224}Ra							
Sta. R	77.21±6.48	108.20±14.3	NA	NA	NA	NA	NA
Sta. 1	45.16±4.29	53.59±5.70	NA	NA	6.03±1.59	6.00±1.07	7.74±1.29
Sta. 2	47.21±4.32	50.13±4.82	NA	21.34±2.68	15.30±1.77	16.73±1.66	9.69±1.03
Sta. 3	47.37±3.87	63.77±6.49	NA	33.16±2.32	29.56±3.22	32.79±3.72	20.34±2.04
Sta. 4	NA	99.42±7.89	NA	30.84±1.57	28.16±2.18	30.14±2.30	6.77±0.87
Sta. 5	7.74±0.75	21.70±2.45	NA	8.81±0.74	9.81±1.29	4.51±0.43	2.85±0.30

	2000						
	26 Jan	16 Feb	13 Mar	19 Apr	23 May	15 Jun	Average
^{226}Ra							
Sta. R	NA	NA	13.40±3.08	NA	NA	13.83±3.37	13.70±0.29
Sta. 1	Ice	Ice	17.60±4.79	16.83±2.41	15.83±2.39	24.15±2.49	25.78±10.3
Sta. 2	26.12±2.83	21.05±1.70	22.64±3.73	33.51±4.67	29.77±3.29	48.11±3.47	36.24±10.7
Sta. 3	21.44±2.31	24.73±8.94	21.43±2.38	30.86±5.75	36.30±3.34	38.35±2.51	33.50±9.31
Sta. 4	23.06±2.40	22.56±4.97	23.42±3.54	21.44±2.68	36.27±4.67	19.30±2.33	29.45±9.67
Sta. 5	13.54±3.36	14.77±1.81	12.07±1.42	13.11±2.55	10.99±2.58	12.23±1.30	14.56±2.13
^{228}Ra							
Sta. R	NA	NA	13.82±3.27	NA	NA	15.83±3.99	41.02±31.9
Sta. 1	Ice	Ice	6.43±1.78	10.14±1.53	11.84±1.88	21.91±2.61	19.93±16.2
Sta. 2	17.20±1.83	29.79±2.65	28.64±4.70	27.89±3.83	9.20±1.00	13.65±1.07	25.09±8.30
Sta. 3	13.97±1.68	20.89±7.58	24.03±2.68	29.87±5.64	35.00±2.94	32.76±2.33	27.29±7.27
Sta. 4	14.97±1.41	15.11±3.30	24.06±3.68	12.47±1.53	25.00±3.06	29.88±3.13	22.87±9.56
Sta. 5	4.52±1.14	5.54±0.69	5.73±0.69	5.56±1.08	6.38±1.48	10.16±1.07	6.64±1.45
^{224}Ra							
Sta. R	NA	NA	24.00±5.58	NA	NA	14.66±3.63	56.01±44.4
Sta. 1	Ice	Ice	4.27±1.18	12.01±1.78	11.56±1.85	24.04±2.54	18.93±18.3
Sta. 2	16.88±1.76	51.62±3.74	20.05±3.27	23.25±3.24	10.03±1.08	17.59±1.30	24.98±15.4
Sta. 3	11.48±1.35	19.71±7.13	21.95±2.51	29.83±5.60	38.89±3.33	89.37±6.94	36.52±21.7
Sta. 4	15.30±1.41	21.61±4.66	32.36±4.86	16.96±2.04	31.75±3.95	65.15±6.60	34.40±26.2
Sta. 5	4.28±1.06	7.27±0.86	4.85±0.60	3.51±0.69	5.30±1.24	15.52±1.52	8.01±5.55

Groundwater—^{226}Ra, temperature, salinity, and nutrient data measured in groundwater samples are listed in Table 3. Groundwater temperature averaged 25.1 ± 2.9°C, whereas salinity was more variable, averaging 19.240 ± 12.992‰. Groundwater nutrient concentrations ranged from 5.32 to 90.26 μM for total dissolved inorganic nitrogen (TDIN = $[NH_4^+] + [NO_3^-] + [NO_2^-]$) and 0.20 to 9.70 μM for dissolved inorganic phosphorus (DIP). Note that groundwater Ra activities are reported in units of dpm L^{-1}, which is 100 times greater than surface water Ra activities in the Pettaquamscutt estuary. Groundwater ^{226}Ra activities from samples near the salt marsh–estuary boundary exhibit significant spatial variability, ranging from 1.7 to 7.0 dpm L^{-1}, averaging 3.9 ± 2.2 dpm L^{-1}.

Groundwater Ra activities are comparable to those from other studies, with slight variations attributed to differences

Table 3. Measurements of temperature, salinity, depth, TDIN, DIP, and ^{226}Ra in the shallow aquifer of the Pettaquamscutt River estuary collected on 8 August 2000.

Station	Temperature (°C)	Salinity (ppt)	Depth (cm)	TDIN (μM)	DIP (μM)	^{226}Ra (dpm L^{-1})
A	22.5	11.664	45	18.85	1.96	3.4
B	24	0.318	30	26.41	0.20	2.1
C	30	23.962	30	90.26	0.23	7.0
D	24	29.728	50	5.32	1.02	5.2
E	25	30.529	40	40.00	9.70	1.7
Average	25±3	19.240±12.992	39±9	36.17±32.73	2.62±4.02	3.9±2.2

in bedrock geology. For the North Inlet salt marsh, Krest et al. (2000) observed ^{226}Ra groundwater activities ranging from 0.16 to 2.18 dpm L^{-1}, and ^{228}Ra activities ranging from 0.36 to 13.29 dpm L^{-1}. Charette et al. (2001) reported a range of 0.24 to 1.6 dpm L^{-1} for ^{226}Ra, and 0.95 to 6.7 dpm L^{-1} for ^{228}Ra in Waquoit Bay. Scott and Moran (2001) observed ^{226}Ra pore-water activities of 5–8 dpm L^{-1} in southern Rhode Island salt ponds.

Discussion

Source of ^{226}Ra and ^{228}Ra to the Pettaquamscutt estuary—Groundwater contains dissolved material produced from the weathering of rock (Adams and Rhodes 1960; Freeze and Cherry 1979; Fanning et al. 1981; Cable et al. 1996; Corbett et al. 1999; Greeman et al. 1999). Several studies have suggested that ^{228}Ra and ^{226}Ra have potential as groundwater source tracers since they have identical chemistries but are from different decay series (King et al. 1982; Greeman et al. 1999; Eikenberg et al. 2001; Tricca et al. 2001). As a result, the ^{228}Ra/^{226}Ra ratio in groundwater is a function of the parent isotope ratio (^{232}Th/^{238}U) in the source bedrock.

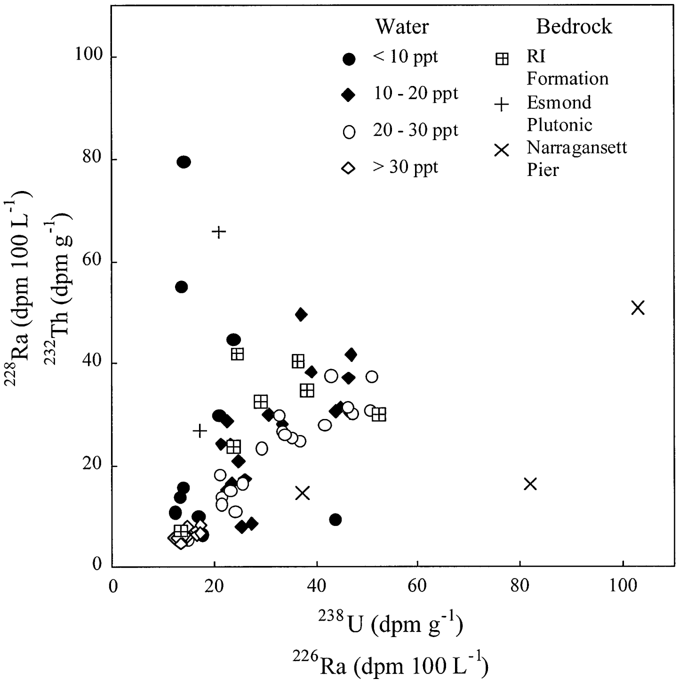

Fig. 3. Bedrock ^{232}Th/^{238}U and water sample ^{228}Ra/^{226}Ra activity ratios. Rock data from Nevins (1991), water data from this study.

The ^{228}Ra/^{226}Ra ratio measured in the Pettaquamscutt estuary suggests that these Ra isotopes are derived from the weathering of the underlying bedrock within the watershed. The bedrock of the Pettaquamscutt watershed is composed of four major types: Rhode Island Formation metasediments, Narragansett Pier granite, Esmond granite gneiss, and Esmond augen granite gneiss (Hermes et al. 1994). Each rock type has a distinct ^{232}Th/^{238}U activity ratio (Nevins 1991). Figure 3 compares the ^{232}Th/^{238}U of the bedrock to the ^{228}Ra/^{226}Ra of the estuary. Nearly all of the water sample ^{228}Ra/^{226}Ra ratios fall within the range of the bedrock ^{232}Th/^{238}U ratios, consistent with the local bedrock as the primary source of long-lived Ra isotopes to the estuary.

The low-salinity ^{228}Ra/^{226}Ra activity ratios exhibit high variability (Fig. 3). Low-salinity samples that trend toward the Esmond granite sample were collected in the summer of 1999, during a drought. Gilbert Stuart Stream was still flowing at this time, and it was likely supported by groundwater. The ^{228}Ra/^{226}Ra ratio suggests the groundwater originated near the topographic high in the northwest section of the watershed, which is characterized by the Esmond granite bedrock. The remaining samples fall within the range of the Rhode Island Formation metasedimentary rock, the largest bedrock component of the watershed.

Radium distribution within the Pettaquamscutt estuary—In the absence of groundwater input, the chemistry of Ra dictates that its distribution within an estuary will be controlled primarily by mixing between riverine and oceanic end members and particle desorption. The calculated distribution of Ra (Ra$_C$; dpm 100 L^{-1}) as a function of salinity can be described using the equation (Krest et al. 1999)

$$\mathrm{Ra}_C = f(\mathrm{Ra}_O) + (1 - f)(\mathrm{Ra}_R) + ((1 - f)\mathrm{Ra}_{\mathrm{des}})(1 - e^{[-S_S/\xi]}) \tag{2}$$

where Ra$_O$ and Ra$_R$ represent the oceanic and riverine end-member Ra activities (dpm 100 L^{-1}), Ra$_{\mathrm{des}}$ represents the desorbable Ra activity, and S_s represents the sample salinity. The symbol ξ represents the salinity at which the particle-bound Ra activity is reduced to e^{-1} of its original activity (Krest et al. 1999). The variable f is the seawater fraction of the sample derived from salinity,

$$f = \frac{(S_S - S_R)}{(S_O - S_R)} \tag{3}$$

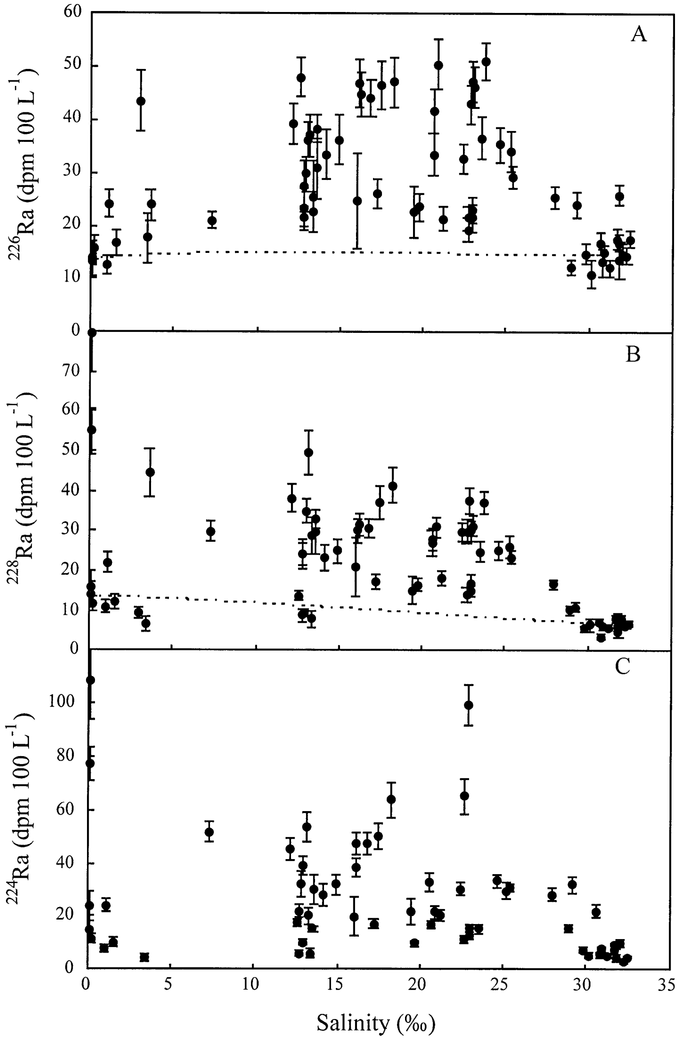

Fig. 4. Radium activities plotted against salinity for (A) ^{226}Ra, (B) ^{228}Ra, and (C) ^{224}Ra. The curves in plots A and B represent model results for average end-member values of ^{226}Ra and ^{228}Ra, respectively.

where S_R and S_O represent the riverine and oceanic salinity end members.

With Eqs. 2 and 3, the distribution of ^{226}Ra within the Pettaquamscutt estuary was calculated using the average ^{226}Ra Sta. R (low salinity) value of 13.7 dpm 100 L^{-1}, the average Sta. 5 (high salinity) activity of 14.6 dpm 100 L^{-1}, a desorbable activity of 1.6 dpm 100 L^{-1} (Scott 1998; Scott and Moran 2001), and a ξ value of 5‰ (Krest et al. 1999). Similarly, the distribution of ^{228}Ra was calculated using an average high-salinity end-member activity of 6.4 dpm 100 L^{-1} and a low-salinity end-member and desorbable activities of 13.6 dpm 100 L^{-1} and 0.96 dpm 100 L^{-1}, respectively. Both low-salinity and desorbable ^{228}Ra activities were estimated using the average Rhode Island Formation bedrock ^{232}Th/^{238}U activity ratio of 0.99 (Nevins 1991) and corresponding ^{226}Ra activities. The calculated distributions of ^{226}Ra and ^{228}Ra are nonconservative (Fig. 4A,B), with a slight enrichment at brackish salinity due to desorption of surface-bound particulate radium.

The calculated distribution of ^{226}Ra and ^{228}Ra is significantly lower than the corresponding measured activities. If particle desorption were to explain the observed enrichment, then this would require a desorbable ^{226}Ra value of approximately 70 dpm 100 L^{-1}. The maximum particle load from Gilbert Stuart Stream, the primary source of riverine particles to the estuary, is assumed to be $<$25 mg L^{-1}. Thus, an upper estimate for the desorbable ^{226}Ra activity is 6.5×10^{-4} dpm mg^{-1} (Scott 1998; Scott and Moran 2001) implies a maximum desorbable ^{226}Ra activity of 1.6 dpm 100 L^{-1}. A suspended sediment load on the order of 10^7 mg L^{-1} would be required for particulate ^{226}Ra desorption to account for the observed ^{226}Ra distribution. A similar calculation indicates that the observed distribution of ^{228}Ra is also inconsistent with a significant contribution from particle desorption. The only remaining source that may account for the observed ^{226}Ra and ^{228}Ra enrichment is input of Ra-enriched groundwater.

Constraining the residence time of Ra within the estuary—Short-lived ^{224}Ra data may be used to constrain the residence time of Ra within the Pettaquamscutt estuary (Hancock and Murray 1996; Torgerson et al. 1996; Rama and Moore 1996; Hancock et al. 2000; Charette et al. 2001). ^{224}Ra is enriched at brackish salinities, analogous to ^{226}Ra and ^{228}Ra (Fig. 4C). This enrichment is attributed to pore-water discharge of Ra into the overlying water column. If there were no groundwater input of ^{224}Ra, then minimal ^{224}Ra would be present within the estuary because the Rhode Island Sound and Gilbert Stuart Stream end members are ^{224}Ra deficient (Fig. 4C). In addition, the fact that ^{224}Ra is detectable indicates that the residence time of the estuary must be $<$5 half-lives of ^{224}Ra, or $<$20 d. If it were longer than 20 d, the ^{224}Ra would have decayed to activities below detection limits.

A further constraint on the residence time of the Pettaquamscutt can be determined from ^{224}Ra and ^{228}Ra distributions. Sediment pore water enriched in ^{224}Ra relative to ^{228}Ra has been reported for many estuaries around the world and represents the primary source of Ra to the estuaries (Webster et al. 1994, 1995; Hancock and Murray 1996; Rama and Moore 1996; Hancock et al. 2000; Charette et al. 2001). Following pore-water discharge to the overlying water, only decay of ^{224}Ra will alter the ^{224}Ra/^{228}Ra ratio in the water column.

The residence time of Ra within the estuary (T, d) can be estimated using (Moore 1997*a*, 2000),

$$\left(\frac{^{224}\mathrm{Ra}_{\mathrm{xs}}}{^{228}\mathrm{Ra}_{\mathrm{xs}}}\right)_{\mathrm{obs}} = \left(\frac{^{224}\mathrm{Ra}}{^{228}\mathrm{Ra}}\right)_{\mathrm{pw}} e^{-\lambda_{224}T} \tag{4}$$

where (^{224}Ra$_{\mathrm{xs}}$/^{228}Ra$_{\mathrm{xs}}$)$_{\mathrm{obs}}$ represents the observed ratio in the estuary, (^{224}Ra/^{228}Ra)$_{\mathrm{pw}}$ represents the estimated pore-water ratio, and λ_{224} represents the decay constant for ^{224}Ra (0.1894 d^{-1}). Excess ^{224}Ra and ^{228}Ra (Ra$_{\mathrm{xs}}$; dpm 100 L^{-1}) are defined as

$$\mathrm{Ra}_{\mathrm{xs}} = \mathrm{Ra}_m - f(\mathrm{Ra}_0) \tag{5}$$

where Ra$_m$ is the measured activity of Ra in a sample, Ra$_o$ is the ocean end member (Sta. 5) for a given sample, and f

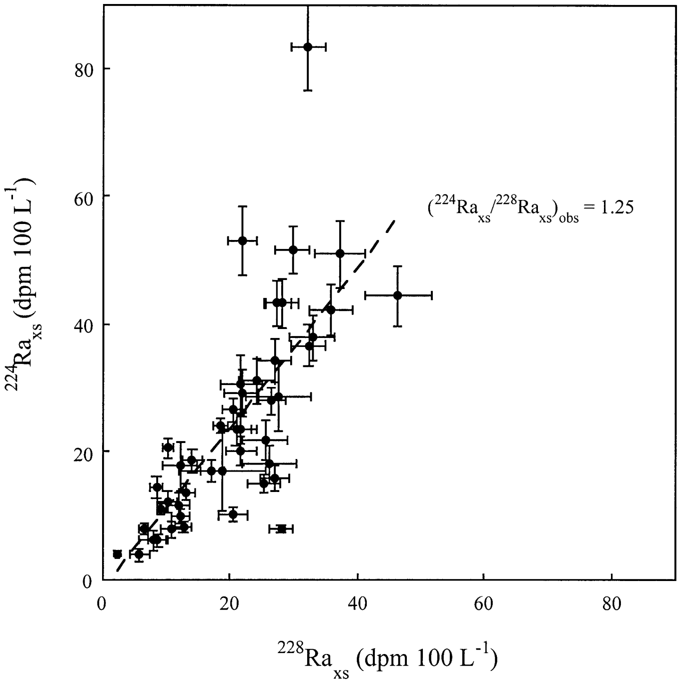

Fig. 5. Plot of $^{224}Ra_{xs}$ against $^{228}Ra_{xs}$ for all samples collected within the estuary. The slope of 1.25 represents the average $^{224}Ra_{xs}/^{228}Ra_{xs}$ ratio determined in the Pettaquamscutt estuary.

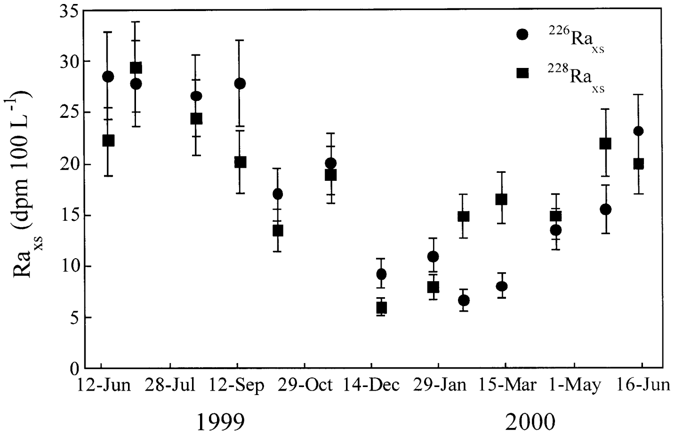

Fig. 6. Seasonal changes in $^{226}Ra_{xs}$ and $^{228}Ra_{xs}$ within the Pettaquamscutt estuary from 1 June 1999 to 30 June 2000.

is defined by Eq. 3. Note that this calculation accounts for the fractional contribution (f) of Rhode Island Sound water that mixes into the estuary. To solve for T, Eq. 4 can be rewritten as

$$T = \frac{\ln\left[\left(\frac{^{224}Ra}{^{228}Ra}\right)_{pw} - \left(\frac{^{224}Ra_{xs}}{^{228}Ra_{xs}}\right)_{obs}\right]}{\lambda_{224}} \qquad (6)$$

The average $(^{224}Ra_{xs}/^{228}Ra_{xs})_{obs}$ ratio observed within the Pettaquamscutt is 1.25 (Fig. 5). It is interesting to note that the high correlation apparent in Fig. 5 must reflect the efficient tidal mixing within the estuary. Owing to a lack of ^{224}Ra groundwater measurements, we use a $(^{224}Ra/^{228}Ra)_{pw}$ ratio of 5.6 reported for Waquoit Bay (Charette et al. 2001), a coastal system that is geologically similar to the Pettaquamscutt. If we assume that pore-water discharge is the primary source of $^{224}Ra_{xs}$, Eq. 6 yields an annual average residence time of 8 d for the Pettaquamscutt estuary. Setting $(^{224}Ra/^{228}Ra)_{pw} = 3$ results in a residence time of 4 d, while using $(^{224}Ra/^{228}Ra)_{pw} = 10$ increases the residence time to 10 d. Thus, we estimate a residence time of 8 ± 4 d. By comparison, as discussed below, using a surface volume of the estuary of 36.9×10^5 m^3, a tidal prism volume of 2.82×10^5 m^3, and a tidal period of 1.91 d^{-1}, a residence time of 7 d is calculated, which is consistent with the ^{224}Ra-derived residence time.

Groundwater input models—Groundwater is defined in this investigation as water that enters the marine environment through the sediments, regardless of its salinity. The input of groundwater can be calculated for each sampling period using a mass balance calculation, whereby the removal of excess Ra from the estuary must be in balance with the input of Ra from groundwater. In this case, excess ^{226}Ra and ^{228}Ra activity (Ra_{xs}; dpm 100 L^{-1}) is defined as

$$Ra_{xs} = Ra_m - Ra_c \qquad (7)$$

where Ra_m represents the measured Ra activity within the estuary and Ra_c represents the model-predicted Ra distribution within the estuary (Eq. 2). A volume-weighted average Ra_{xs} value ($\overline{Ra}_{xs}$) for the entire estuary was then determined for each month based on the geographic station distribution (Fig. 1, Table 1). The $\overline{Ra}_{xs}$ varied on a monthly basis for both ^{226}Ra and ^{228}Ra (Fig. 6). Highest values of $^{226}\overline{Ra}_{xs}$ were calculated for the summer of 1999, ranging from 26 to 28 dpm 100 L^{-1}, compared with lowest values in the winter, ranging from 6 to 9 dpm 100 L^{-1}. Similar results for $^{228}\overline{Ra}_{xs}$ were also calculated (Fig. 6).

Two methods were used to quantify the removal flux of Ra. The first considers daily tidal circulation as controlling flushing, which is reasonable for the portion of the Pettaquamscutt south of Sta. 3. The primary assumption in this case is that the tidal prism is well mixed and that discharged water represents the average composition of the entire estuary. The second method considers the estuary to be a discrete body of water with a residence time longer than the tidal period, which is appropriate for the estuary north of Sta. 3. This method assumes that the ^{224}Ra-derived residence time is representative of the entire estuary.

Using the tidal prism method, the removal flux of Ra from the estuary (J_{Ra}; dpm m^{-2} d^{-1}) is calculated using (Krest et al. 2000)

$$J_{Ra} = \frac{\overline{Ra}_{xs} \times \forall \times \tau \times 10}{A_E} \qquad (8)$$

where $\forall$ represents the tidal prism of the estuary (m^3), τ represents the tidal period (1.91 d^{-1}) (Gaines 1975), and A_E represents the area of the estuary (m^2) (the factor of 10 corrects for the conversion from dpm 100 L^{-1} to dpm m^{-3}). Eq. 8 was modified due to the absence of Ra data from Pettaquamscutt Cove by removing the area and tidal prism (~65% of the total tidal prism) attributed to the Cove; we

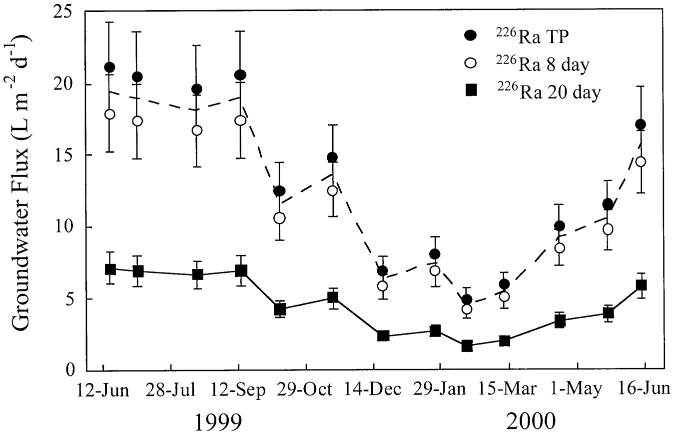

Fig. 7. Seasonal groundwater input derived from ^{226}Ra to the Pettaquamscutt watershed from 1 June 1999 to 30 June 2000 using tidal prism (TP), T = 8 d (8 d) and T = 20 (20 d) calculations. Dashed line represents the average between the tidal prism and T = 8 d flux.

used a reduced A_E of 1.89 × 10^6 m^2 (Table 1) and ∀ of 2.82 × 10^5 m^3. The new ∀ value was determined using tidal elevation data and the area of the estuary exclusive of the Cove (Gaines 1975; Siffling 1997).

With the residence time method, the removal flux of Ra from the Pettaquamscutt is estimated using

$$J_{\mathrm{Ra}} = \frac{\overline{\mathrm{Ra}}_{\mathrm{xs}} \times V_E \times 10}{T \times A_E} \tag{9}$$

where V_E represents the exchangeable volume of the estuary (m^3), and T represents the residence time of Ra within the estuary. Both the calculated residence time of 8 d (T = 8 d) and a maximum value of 20 d (T = 20 d) were used. Because the surface mixed layer is only 3-m deep in the ponds (Gaines 1975; Scranton et al. 1995), a value of 3.69 × 10^6 m^3 was used for V_E (Table 1).

If we assume that the removal of Ra from the sample site is in steady state with respect to groundwater input, the groundwater flux (F_{GW}; L m^{-2} d^{-1}) can be calculated using

$$F_{\mathrm{GW}} = \frac{J_{\mathrm{Ra}}}{[\mathrm{Ra}_{\mathrm{GW}}]} \tag{10}$$

where $[\mathrm{Ra}_{\mathrm{GW}}]$ represents the average groundwater ^{226}Ra activity of 3.9 dpm L^{-1} (Table 3). An average ^{228}Ra groundwater activity of 3.9 dpm L^{-1} was determined using the average ^{232}Th/^{238}U activity ratio for the Rhode Island Formation bedrock (0.99), which is the most abundant bedrock type in the Pettaquamscutt watershed (Nevins 1991).

Based on the tidal prism method, the Ra-derived input of groundwater to the Pettaquamscutt estuary ranges from 4.4 to 22 L m^{-2} d^{-1} (Fig. 7). Using the residence time approach, the groundwater input ranges from 3.7 to 18 L m^{-2} d^{-1} with T = 8 d and 1.5 to 7.4 L m^{-2} d^{-1} with T = 20 d (Fig. 7). Results from both calculations bracket those previously reported for the Pettaquamscutt and other coastal regimes (Table 4). Moreover, the Ra-derived fluxes clearly vary on a seasonal basis, with the highest groundwater inputs calculated for the summer of 1999 and the lowest values calculated for the winter of 1999–2000 (Table 5, Fig. 7).

Results calculated using the residence time method with T = 8 d and the tidal prism model differ from those using T = 20 d by a factor of 3 (Table 4). The difference between the tidal prism and T = 20 d results suggests that approximately one-third of the tidal prism originates and remains within the estuary over a tidal cycle. Therefore, because the tidal prism method assumes that the tidal exchange is complete, it provides an upper estimate for the removal flux of Ra. Owing to constant tidal flushing, however, the residence time of water in the estuary south of station Sta. 3 must be <20 d. In fact, the residence time of water within the Pettaquamscutt must be shortest near station Sta. 5, at the opening to Rhode Island Sound, and increase with distance away from the mouth. The residence time estimate of 20 d may be more representative of the upper and lower ponds, though it is not evenly distributed through the estuary as a whole. Unlike the other two calculations, the annually averaged ^{224}Ra-derived residence time of 8 d integrates the lower and upper estuary, as indicated by the nearly constant $^{224}\mathrm{Ra}_{\mathrm{xs}}$/$^{228}\mathrm{Ra}_{\mathrm{xs}}$ ratio observed throughout the estuary. This integration accounts for the rapid flushing of the lower estuary and slower flushing of the upper estuary. Therefore, using T = 8 d may provide the most representative estimate of the Ra removal flux and hence groundwater input.

In some cases, the ^{228}Ra-derived groundwater fluxes are slightly different than the ^{226}Ra-derived fluxes (Table 5). This may be a function of the variable ^{232}Th activities in the underlying bedrock, which can influence ^{228}Ra activities in two ways. First, the Rhode Island Formation bedrock in the Pettaquamscutt valley is composed of a blend of different me-

Table 4. Radium-derived groundwater fluxes in the Pettaquamscutt River estuary and other coastal areas.

Study area	Groundwater flux (L m^{-2} d^{-1})	Source
Pettaquamscutt River estuary	4.4–22	This study, tidal prism (7 d)
	3.7–18	This study, Ra residence time (8 d)
	1.5–7.4	This study, Ra residence time (20 d)
	0.5–15	De Meneses (1990)
South Coastal Ponds, RI	7.1–19	Scott and Moran (2001)
Waquoit Bay, MA	9.5	Charette et al. (2001)
North inlet, SC	31	Krest et al. (2000)

Table 5. Seasonal radium-derived groundwater flux averages, total annual input, and recharge estimate for the Pettaquamscutt River estuary from 1 June 1999 through 30 June 2000.

	Summer 1999	Fall 1999	Winter 1999–2000	Spring 2000	Total input
	(L m^{-2} d^{-1})				(L yr^{-1})
Tidal prism (7 d)					
^{226}Ra	20.1±1.1	15.9±4.2	5.8±2.1	11.1±4.8	9.4×10^9
^{228}Ra	19.0±3.2	13.2±3.2	6.9±3.2	13.8±2.1	9.3×10^9
Ra residence time (8 d)					
^{226}Ra	17.3±0.6	13.5±3.5	5.6±1.4	9.4±3.9	7.9×10^9
^{228}Ra	15.9±2.3	11.0±2.2	6.0±2.9	11.5±2.0	7.9×10^9
Ra residence time (20 d)					
^{226}Ra	6.87±0.53	5.29±1.06	2.12±0.53	3.70±1.59	3.2×10^9
^{228}Ra	6.35±0.53	4.23±0.53	2.65±1.06	4.76±0.53	3.2×10^9
Recharge estimate					10×10^9

tasedimentary rocks (Hermes et al. 1994), each having unique ^{238}U and ^{232}Th activities (Nevins 1991). If the source of groundwater varied over the study period, the groundwater ^{228}Ra/^{226}Ra activity ratio may have also varied. The models used in this investigation do not account for variations in groundwater ^{228}Ra activity. Second, the low-salinity end-member ^{228}Ra activity will vary with the extent of stream flow supported by groundwater. ^{228}Ra activities in freshwater were elevated during dry periods, when the stream may have been supported by groundwater from ^{232}Th-enriched bedrock. We assumed an average value for the freshwater ^{228}Ra activity, which may not account for possible changes in the source (runoff vs. groundwater) of the stream water.

Groundwater recharge balance—A quantitative test of the application of ^{226}Ra and ^{228}Ra as tracers of submarine groundwater discharge can be made by comparing aquifer recharge from precipitation to the Ra-derived groundwater input to the Pettaquamscutt estuary. The total volume of groundwater input to the estuary on an annual basis can be calculated by multiplying the groundwater flux by a time constant and the area of the estuary. The time constant was defined as the midpoint between three consecutive sampling periods, ranging from 18 to 36 d (average = 30 ± 5 d). Again, the area of Pettaquamscutt Cove was subtracted from the total area of the estuary to yield 1.89 × 10^6 m^2. The calculated groundwater flux was then extrapolated over this area and time interval to determine the volume input. Values for each period were summed to provide the total groundwater input over the entire 13-month study and normalized to 1 year. With ^{226}Ra, an annual input of 9.4 × 10^9 L was calculated using the tidal prism approach, and a groundwater discharge of 7.9 × 10^9 L was calculated using $T = 8$ d and a discharge of 3.2 × 10^9 L was calculated using $T = 20$ d (Table 5). The ^{226}Ra-derived fluxes are consistent with the respective ^{228}Ra results.

The discharge of groundwater must be in balance with the recharge of the surrounding aquifer. Precipitation is the primary form of aquifer recharge for the Pettaquamscutt watershed. The volume of precipitation available to recharge the aquifer (P_R; L) is

$$P_R = A_W \times \sum P \times \Phi \tag{11}$$

where A_W is the total watershed area (Table 1), P is the total input of precipitation (mm), and Φ is a dimensionless parameter that accounts for loss of precipitation via surface runoff and evapotranspiration. The Pettaquamscutt watershed received roughly 1,360 mm of precipitation from 1 June 1999 to 30 June 2000 (Kingston, Rhode Island; www.cdo.ncdc.noaa.gov). In Southern Rhode Island, a reasonable value for Φ is 0.5 (Veeger 2001, pers. comm.). Considering the sample distribution and the topography of the watershed, certain areas were eliminated from the recharge estimate. Specifically, the watershed adjacent to Pettaquamscutt Cove was not included because its topography suggests all recharge would discharge to the Cove (Fig. 1). Also, the topography of the upper watershed indicates that recharge at this location will discharge into Gilbert Stuart Stream, which was neglected. The remaining area is 145 × 10^5 m^2 (Table 1), which is <50% of the total watershed area. Using these data, aquifer recharge to the Pettaquamscutt estuary during the sample period was estimated to be 10 × 10^9 liters (Table 5).

The calculated aquifer recharge compares well with the Ra-derived groundwater fluxes using the tidal prism approach and residence time method using $T = 8$ d; however, the calculated groundwater input was a factor of three lower with $T = 20$ d (Table 5). Although there is good agreement between the tidal prism approach and the aquifer recharge estimates, the tidal prism calculation provides a maximum estimate of groundwater input. Using the lower estimate from the 20-d residence time calculation, only ~32% of the recharge water is traced by Ra, whereas this value increases to ~80% using a residence time of 8 d. That the Ra-derived groundwater fluxes are lower than the recharge estimate may be attributed to a fraction of groundwater entering the estuary without passing through the saline aquifer and therefore not transporting dissolved Ra into the estuary.

Several assumptions should be noted regarding the aquifer recharge calculations. In particular, the Φ factor used in the recharge calculation represents an annual average. Owing to the unusually intense drought in the summer of 1999, evapotranspiration, which contributes to Φ, was likely to have

Table 6. Groundwater input and groundwater-derived nutrient input to the Pettaquamscutt River estuary and other coastal systems. Point Judith, Potter, Green Hill, and Ninigret salt ponds are located in southern Rhode Island (Scott 1998; Scott and Moran 2001). NR = not reported.

Location	Area ($\times 10^5$ m^2)	GW input ($\times 10^9$ L yr^{-1})	GW TDIN (μM)	GW DIP (μM)	TDIN flux (mmol m^{-2} yr^{-1})	DIP flux (mmol m^{-2} yr^{-1})	N : P
Pettaquamscutt, tidal prism (7 d)	18.9	9.4	36.2	2.62	180	13	13.8
Pettaquamscutt, Ra residence time (8 d)	18.9	7.9	36.2	2.62	151	11	13.8
Pettaquamscutt, Ra residence time (20 d)	18.9	3.2	36.2	2.62	61	4.4	13.8
Point Judith	78.5	20	264	0.40	673	1.0	660
Potter	13.5	9.1	264	0.40	1780	2.7	660
Green Hill	15.5	8.0	264	0.40	1363	2.1	660
Ninigret	64.5	17	264	0.40	696	1.1	660
North Inlet, SC	340	390	77*	29	883	333	2.7
Waquoit Bay, MA	39	14	58	NR	208	—	—

* NH_4^+ only.

been above average and so the recharge estimate may be a maximum value. Glacial till sediments that fringe portions of the watershed have low permeability, which reduces aquifer recharge (Hahn 1959; Johnson and Marks 1959; Lang 1961). There are also several small streams that discharge to the Pettaquamscutt (Fig. 1), which may have been supported by groundwater. Groundwater input from these streams may not be traced by Ra and not be included in the overall radium-derived groundwater input. The fact that the Ra-derived groundwater estimates do not exceed the aquifer recharge on an annual basis is encouraging, however, a fact which suggests that Ra isotopes are useful tracers of groundwater input to this coastal system.

Groundwater nutrient fluxes—The supply of nutrients from groundwater to the Pettaquamscutt estuary can be calculated by multiplying the groundwater flux by the groundwater nutrient concentrations (TDIN and DIP), which were determined in the adjacent shallow salt marsh aquifer. With the total Ra-derived groundwater input over the 13-month study period normalized to 1 year (9.4×10^9 L) from the upper estimate tidal prism approach and the nutrient concentrations listed in Table 6, approximately 180 mmol TDIN m^{-2} yr^{-1} and 13 mmol DIP m^{-2} yr^{-1} were input to the Pettaquamscutt (Table 6). With $T = 8$ d, approximately 151 mmol TDIN m^{-2} yr^{-1} and 11 mmol DIP m^{-2} yr^{-1} were input to the Pettaquamscutt. The lower groundwater flux estimate, using $T = 20$ d, yields an input of 61 mmol TDIN m^{-2} yr^{-1} and 4.4 mmol DIP m^{-2} yr^{-1}.

It is interesting to compare the groundwater nutrient fluxes calculated for the Pettaquamscutt estuary with similar estimates made for several coastal ponds (Point Judith, Potter, Green Hill, and Ninigret) located in southern Rhode Island. Groundwater nutrient concentrations were recently determined for shallow wells near these ponds ($n = 5$) by Scott (1998), which were then multiplied by the ^{226}Ra-derived groundwater fluxes to these ponds reported by Scott and Moran (2001); results of these calculations are also presented in Table 6. Dissolved nutrient fluxes from groundwater to these coastal ponds range from 673 to 1,780 mmol m^{-2} yr^{-1} for TDIN and 1.0 to 2.7 mmol m^{-2} yr^{-1} for DIP. Despite the similar groundwater fluxes, these coastal ponds are characterized by a substantially larger total input of nitrogen and smaller inorganic phosphorus flux compared to the Pettaquamscutt, which suggests a significant difference in the corresponding groundwater nutrient reservoirs. In addition, Ra-derived nutrient fluxes to the Pettaquamscutt are similar to Waquoit Bay (TDIN flux only) and lower than for North Inlet Salt Marsh (Table 6), of which the latter may reflect a larger groundwater nutrient reservoir.

Groundwater nutrient input would also be expected to vary seasonally, which may have implications for seasonal phytoplankton blooms. Dissolved nitrogen and phosphorus are input to the Pettaquamscutt at a ratio of ~14 : 1, which is close to the Redfield ratio of 16 : 1 (Table 6). The implication is that, for the Pettaquamscutt, nutrients are stoichiometrically balanced to be readily incorporated by phytoplankton. Based on the Redfield C : N ratio of 6.6 : 1 (Berner and Berner 1996; Pilson 1998) and assuming that all TDIN is converted to phytoplankton biomass, primary production may incorporate as much as 1,188 mmol C m^{-2} yr^{-1} using the tidal prism groundwater flux and 997 mmol C m^{-2} yr^{-1} using $T = 8$ d. Interestingly, these results are similar to a value of 1,350 mmol C m^{-2} yr^{-1} recently reported for Waquoit Bay (Charette et al. 2001).

In addition, phytoplankton surveys conducted on the Pettaquamscutt have observed blooms during spring and late summer (Hanisak 1973; Menezes 2000 pers. comm.). Results from this study suggest an increase in groundwater flux in the spring relative to the winter, with maximum values in the early summer. Groundwater nutrient input may follow a similar trend, and it is possible that seasonal increases in groundwater nutrient input may influence the occurrence of bloom events through the annual cycle.

Conclusions

Measurements of the naturally occurring radionuclides ^{226}Ra and ^{228}Ra have provided new constraints on the supply of groundwater to the well-mixed Pettaquamscutt estuary. Activities of these tracers were determined to be in excess of values calculated using a model that considers mixing and particle desorption, implying a significant input of Ra from groundwater to the Pettaquamscutt. Moreover, the observed seasonal changes in excess Ra activity indicate seasonal changes in groundwater input. ^{228}Ra/^{226}Ra activity ratios within the estuary were similar to ^{232}Th/^{238}U activity ratios in surrounding bedrock, which is consistent with the source of Ra from the weathering of the underlying bedrock and subsequent transport of dissolved ^{226}Ra and ^{228}Ra via groundwater to the estuary. Measurements of the distribution of ^{224}Ra indicate a mean residence time of Ra within the estuary of 8 ± 4 d, with a maximum value of 20 d.

With these Ra data and a simple box model, groundwater input was calculated to be highest in the summer of 1999, lowest in the winter of 1999–2000, and intermediate in the fall of 1999 and spring of 2000. The seasonal range in groundwater flux ($\sim$1.5–22 L m^{-2}d^{-1}) brackets values previously reported for this system and other local coastal ponds and is consistent with estimates of aquifer recharge over an annual cycle using a tidal prism model and an estuarine residence time of 8 d.

Based on these Ra-derived groundwater fluxes and groundwater nutrient concentrations, the input of inorganic nitrogen and phosphorus from groundwater to the Pettaquamscutt was calculated to range from 61 to 180 mmol m^{-2} yr^{-1} and 4.4 to 13 mmol m^{-2} yr^{-1}, respectively. Seasonal changes in groundwater nutrient input may influence the occurrence of phytoplankton bloom events in this coastal system through the annual cycle.

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