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# Utility of radium isotopes for evaluating the input and transport of groundwater-derived nitrogen to a Cape Cod estuary

*Abstract*—Because of rapid increases in population, anthropogenic sources of nitrogen have adversely impacted the water quality of coastal ponds on Cape Cod. A major source of ''new'' nitrogen to these estuaries is groundwater, which intercepts septic tank fields in its flow path to the coastline. Many attempts have been made to quantify this process; however, groundwater discharge is often patchy in nature and is therefore difficult to study by use of traditional techniques such as seepage meters. In Waquoit Bay, MA, we tested an approach based on radium, which is naturally enriched in aquifer fluids and has four isotopes with half-lives ranging from 4 d to 1600 yr. Groundwater entering the bay was low in salinity and contained several orders of magnitude greater radium and dissolved inorganic nitrogen (DIN) relative to ambient bay water. Using a mass-balance approach for radium, we calculated a submarine groundwater flux of ~37,000 $m^3 d^{-1}$, which compared well with aquifer recharge rates calculated from rainfall. From the DIN content of the groundwater, we estimated that ~2100 mol N $d^{-1}$ was directly input to the estuary. However, this nitrogen flux was small in comparison with literature values for DIN fluxes from the heavily populated subestuaries. Furthermore, our results suggest that groundwater flux of DIN was assimilated by plant biomass during the summer but may be exported from the embayment to coastal waters during the winter months.

The importance of coastal groundwater discharge in delivering dissolved nutrients, such as nitrate and phosphate, to coastal waters has often been overlooked, primarily because it is difficult to estimate (Johannes 1980; Nixon et al. 1986; Simmons 1992). The problem lies in the fact that the flow of groundwater through coastal marine sediments, called submarine groundwater discharge (SGWD), is difficult to quantify by use of traditional methods such as seepage meters, since the discharge is often patchy and may vary with time. Unlike rivers, submarine fluid discharge bypasses the estuary filter, which is an important mechanism for contaminant removal in many coastal settings (Moore and Shaw 1998). Even if SGWD rates are modest, dissolved nutrient concentrations in groundwater may be sufficiently high to have a significant impact on the nutrient budgets for receiving waters. Recently, radium has been shown to be a useful chemical indicator of SGWD and, having four isotopes with half-lives ranging from 4 d to 1600 yr, can be used to estimate rates of SGWD on a wide range of timescales (Moore 1996; Rama and Moore 1996).

A key biogeochemical problem associated with coastal groundwater flow on Cape Cod is the introduction of ''new'' nitrogen entrained by groundwater plumes as they pass through septic tank fields located along the coastline (Weiskel and Howes 1991; Valiela et al. 1992). As a result, nitrate concentrations in groundwater may be several orders of magnitude greater than those in the receiving waters (Valiela et al. 1990, 1992; Andrews et al. 1999). Here, we present a study of SGWD in Waquoit Bay, MA utilizing radium isotopes as tracers of SGWD-derived dissolved inorganic nitrogen (DIN) flux to the estuary. Last, we compare these results with productivity estimates from the literature in an attempt to determine whether the estuary is a net source of nutrients to coastal waters.

*Study area*—Waquoit Bay is an enclosed estuary located on the south shoreline of Cape Cod, MA (Fig. 1). Its watershed comprises nearly 65 $km^2$, extending roughly 10 km north from the head of the bay. The bay, on average, is relatively shallow with a mean depth of 1 m; major freshwater sources include the Quashnet River (to the east) and the Childs River (to the west). In terms of the total freshwater budget, these rivers are a minor component, compared with direct groundwater discharge (Cambareri and Eichner 1998).

Hydrologically, Cape Cod is a surficial aquifer system consisting mainly of fine to coarse sand and gravel. Because of the highly permeable nature of the aquifer, an estimated 45% of annual precipitation becomes groundwater recharge (Olcott 1995). Hydraulic conductivity ranges from ~10 to 317 m $d^{-1}$ and averages 91 m $d^{-1}$ in the vicinity of the study area (Cambareri and Eichner 1998). Along its flow path, groundwater is discharged either to surface ponds, estuaries, or the coastal ocean.

Groundwater-derived nutrients from private septic systems have led to increased eutrophication within in this watershed (Valiela et al. 1992). Detailed salinity measurements in the upper bay revealed a strong salinity gradient originating along the shoreline in the absence of riverine input consistent with a SGWD source (Fig. 2a). Also, a recent seepage meter study by MIT colleagues documented flow of submarine fluid discharge at the head of the bay (C. Harvey pers. comm.).

Eutrophication in Waquoit Bay has been directly linked to sewage-derived nitrogen inputs via direct groundwater discharge to the estuary (Valiela et al. 1990; McClelland et al. 1997). The coarse, unconsolidated sands that characterize this watershed contribute significantly to the rapid transport of nutrients to coastal waters. The most notable ecological impact has been a decline in shellfish population and sea grass coverage. The former is likely due to the seasonal decline in dissolved oxygen. The latter is caused by secondary effects, namely an increase in epiphytes which intercept light from their growth substrate, eel grass blades (Valiela et al. 1992).

*Methods*—Samples from Waquoit Bay and adjacent groundwater wells were collected in mid-July 1999. Filtered (1 $\mu$m) seawater samples (100 liters) were collected from 1 m in polypropylene barrels by use of a deck-board pump; radium isotopes were then extracted on a column of Mn-impregnated acrylic fibers (flow rate ~1 liter $min^{-1}$). Groundwater radium samples (~10–20 liters) at the head of the bay were obtained by use of drive-point piezometers and a hand-operated pump. These small-volume samples were

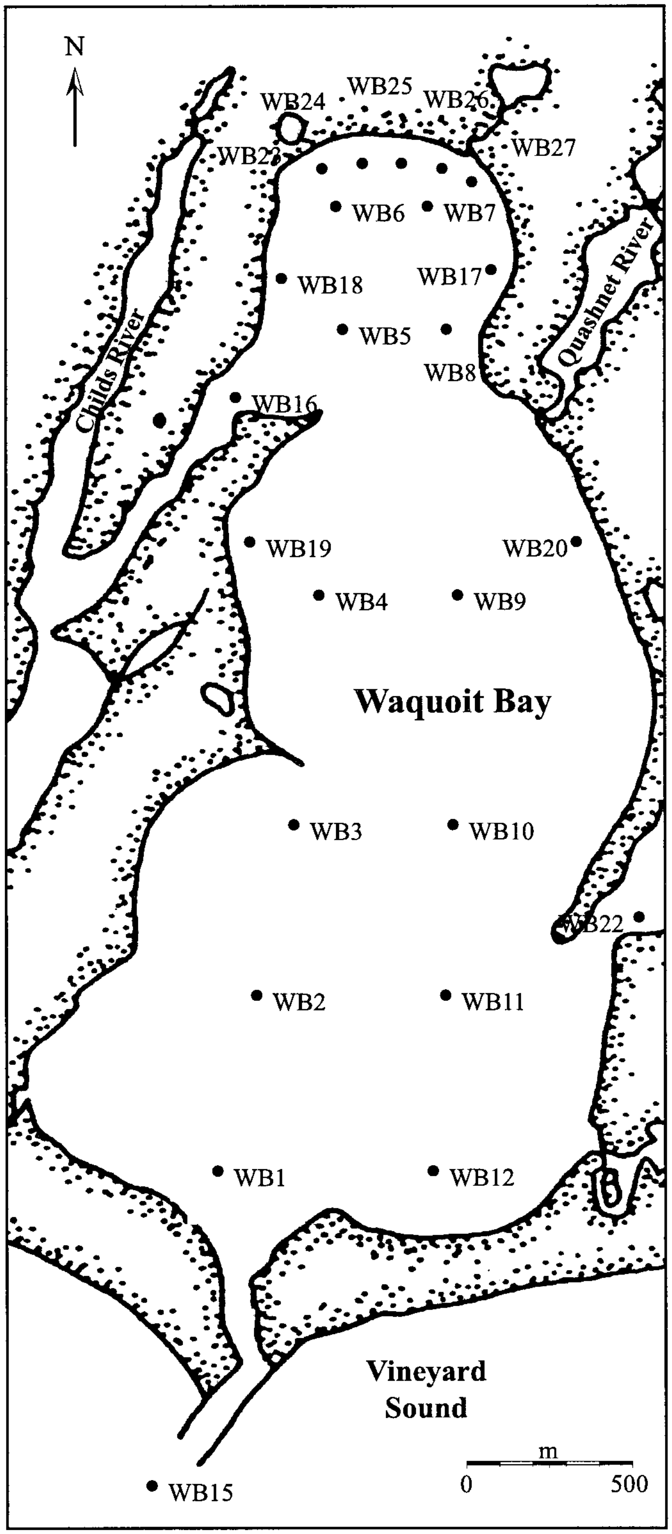


Fig. 1. Map of the study region with the location of water column stations. Not shown are the locations of stations WB14 and WB21, located 1 km due south, and WB13, located 2 km due south of the Bay. Groundwater samples (GW1–15), also not shown, were collected by use of drive-point piezometers from various locations along the head of the bay.

gravity fed through the Mn-fibers. Upon return to the lab, the fibers were partially dried and placed in a delayed coincidence counter for measuring $^{223}Ra$ and $^{224}Ra$ (Moore and Arnold 1996). Then the Mn fibers were ashed at 820°C for 16 h, homogenized, and placed in counting vials. The ash was placed in a well-type gamma spectrometer to measure $^{226}Ra$ and $^{228}Ra$ activities. Each detector was standardized by use of NIST-certified SRMs prepared in the same geometry as the samples. The short-lived radium isotopes ($^{223}Ra$ and $^{224}Ra$) were decay-corrected to the time of sampling; propagated errors on these measurements were <10%.

Subsamples for dissolved nutrients and salinity were collected at each station. Nutrient samples were collected in acid-cleaned polyethylene bottles and frozen until analysis. A suite of nutrients ($NO_3^-/NO_2^-$, $NH_4^+$, $PO4_3^-$, and $SiO_4^-$) was quantified via AutoAnalyzer. Here, we report on only the DIN which we define as the sum of the $NO_3^-/NO_2^-$ plus $NH_4^+$ result for each station. Salinity samples were stored in glass bottles and analyzed by use of a Guideline AutoSal salinometer.

*Results*—Presented in Tables 1 and 2 are DIN concentration and radium isotopic activities for Waquoit Bay water column stations and groundwaters, respectively. The average DIN concentration was low (0.45 $\pm$ 0.24 $\mu$M) for the bay and offshore waters. Ammonium (not shown), a common byproduct of decomposition and heterotrophic respiration, accounted for the majority of DIN (>80%) in the bay averaging 0.37 $\pm$ 0.22 $\mu$M.

Both short- and long-lived radium isotopes were highly correlated in all water-column samples suggesting they originated from similar sources. Radium isotopes generally tracked salinity changes in the bay. Their negative correlation with salinity indicates that the source is freshwater (Fig. 2). Radium activities were highest at the head of the bay and decreased with distance south, and decreased outside the bay, consistent with groundwater discharge (Andrews et al. 1999).

Local groundwater DIN concentrations and radium activities were typically one to four orders of magnitude higher than average Waquoit Bay samples (Table 2). Collected by use of drive-point piezometers <1 m above the high-water mark, these samples ranged in salinity from 0.1–10.6 ppt. Though separated in distance by <100 m, the total DIN concentration of these samples was variable, ranging from 1 to 120 $\mu$M, whereas radium isotopic values remained consistently high. Unlike water column samples, the majority of the DIN in groundwater was as $NO_3^-$.

*Discussion*—Building on the recent pioneering work by W. S. Moore and coworkers, we approached this study with the assumption that radium isotopes would provide useful information on groundwater discharge to this coastal embayment (Moore 1996, 1997; Rama and Moore 1996; Krest et al. 1999; Krest et al. 2000). Three factors make radium a useful tracer of SGWD and associated dissolved chemical species: (i) it is naturally enriched in coastal groundwater relative to seawater (Moore 1996); (ii) it has four isotopes with half-lives ranging from 4 d to 1600 yr; and, (iii) it behaves conservatively once released into marine waters. If we can use radium to quantify the fluxes of SGWD, then,

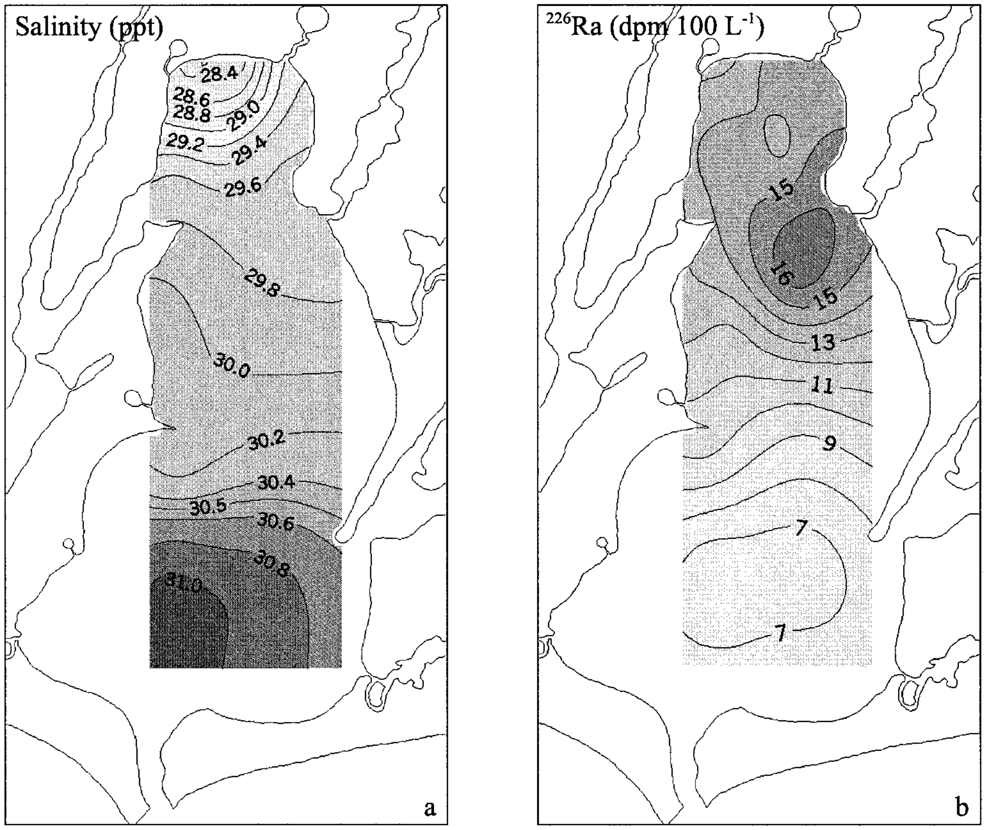


Fig. 2. Contour plots for (a) salinity (ppt) and (b) $^{226}$Ra (dpm 100 L$^{-1}$) in the Waquoit Bay water column during the study period. All four radium isotopes followed a similar pattern ($^{228}$Ra vs. $^{226}$Ra: $R^2 = 0.91$; $^{223}$Ra vs. $^{224}$Ra: $R^2 = 0.90$).

through the measurement of nutrient concentrations in coastal groundwaters, we will be able to construct a mass balance model to estimate fluxes of these nutrients via SGWD.

*Water-mass ages determined from radium isotopes*—The residence time of water in an estuary ($T_w$) is a complex function of topography, tidal range, and external inputs. In estuaries with slow flushing rates, nutrients are retained and can lead to eutrophication. In contrast, a well-flushed embayment will likely be a source of nutrients to offshore waters. In Waquoit Bay, we expect relatively slow flushing rates because of restricted tidal flushing through the narrow inlet to Vineyard Sound (Fig. 1).

The large-scale input of radium isotopes along the boundaries of the bay is akin to a purposeful tracer release, with the short-lived radium isotopes providing the rate of dispersion based on their decay as they mix away from the source. To calculate $T_w$, we chose an approach based on the ratio of $^{223}$Ra/$^{228}$Ra in groundwaters relative to that found in the estuary (Moore 2000):

$$\left[\frac{^{223}\text{Ra}}{\text{ex}^{228}\text{Ra}}\right]_{\text{obs}} = \left[\frac{^{223}\text{Ra}}{\text{ex}^{228}\text{Ra}}\right]_i e^{-\lambda_{223} T_w} \qquad (1)$$

where $[^{223}\text{Ra}/\text{ex}^{228}\text{Ra}]_i$ is the activity ratio of the end-member groundwaters ($0.20 \pm 0.06$) and $[^{223}\text{Ra}/\text{ex}^{228}\text{Ra}]_{\text{obs}}$ is the activity ratio in the sample(s) of interest, in our case, the average for Waquoit Bay. This method is based on the decay rate of $^{223}$Ra relative to $^{228}$Ra, which corrects for mixing effects (Moore 1997), and on the assumption that the initial $^{223}$Ra/ex$^{228}$Ra ratio is constant (Rama and Moore 1996). Since the open ocean contains measurable activities of $^{228}$Ra (but relatively little $^{223}$Ra), we normalize $^{223}$Ra to ex$^{228}$Ra, which is simply the observed activity minus the oceanic end-member ($^{228}\text{Ra}_{\text{end-member}} = 6.4$ dpm 100 L$^{-1}$; unpublished data from the Mid-Atlantic Bight south of Cape Cod).

We used equation (1) to calculate a water-mass age for each station, which yielded an average water-mass age of 9.4 d for Waquoit Bay. A midbay salinity gradient appears to be a barrier to mixing between the upper and lower bay. Combined with the greater tidal-exchange through the inlet to Vineyard Sound (i.e., exchange with ''older'' offshore waters), these two factors produced a higher lower bay $T_w$ of 11 versus 8.8 d for the upper bay. Diffusion of regenerated sedimentary $^{223}$Ra is likely small, compared with to the advective flux from SGWD (Hancock and Murray 1996; Rama and Moore 1996). If it were significant, it would make these calculations lower-limit estimates. Finally, errors associated with these ages can be improved by adding additional end-member (i.e., groundwater) $^{223}$Ra/ex$^{228}$Ra measurements.

Table 1. Dissolved inorganic nitrogen (DIN) and radium isotopic data for Waquoit Bay stations.*

| Station | Salinity (ppt) | DIN ($\mu$M) | $^{224}$Ra† | $^{223}$Ra† | $^{226}$Ra† | $^{228}$Ra† |
|---|---|---|---|---|---|---|
| WB1 | 31.132 | 0.42 | 18.3 | 1.2 | 7.5 | 26.5 |
| WB2 | 31.086 | 0.46 | 28.5 | 1.6 | 6.2 | 27.4 |
| WB3 | 29.919 | 0.40 | 52.6 | 2.7 | 10.8 | 39.3 |
| WB4 | 29.159 | 0.31 | N/A‡ | N/A | 11.4 | 32.2 |
| WB5 | 29.318 | 1.16 | 76.9 | 6.0 | 15.2 | 53.8 |
| WB6 | 29.704 | 0.79 | 78.0 | 4.7 | 11.6 | 44.6 |
| WB7 | 30.342 | 0.43 | 77.3 | 4.8 | 14.0 | 45.2 |
| WB8 | 29.711 | 0.38 | 72.1 | 5.3 | 11.0 | 45.8 |
| WB9 | 29.744 | 0.36 | 64.2 | 5.9 | 18.4 | 76.7 |
| WB10 | 30.111 | 0.31 | 50.8 | 3.3 | 9.1 | 28.9 |
| WB11 | 30.994 | 0.34 | 31.9 | 3.4 | 5.7 | 16.7 |
| WB12 | 30.786 | 0.29 | 43.9 | 3.7 | 8.3 | 27.9 |
| WB13 | 31.485 | 0.39 | 13.1 | 0.8 | 4.3 | 11.6 |
| WB14 | 31.431 | 0.95 | 18.0 | 2.0 | 6.6 | 20.7 |
| WB15 | 31.021 | 0.31 | 19.9 | 2.3 | 7.8 | 21.1 |
| WB16 | 29.605 | 1.00 | 26.9 | 2.8 | 12.1 | 45.2 |
| WB17 | 29.549 | 0.53 | 91.7 | 6.8 | 17.6 | 64.3 |
| WB18 | 29.793 | 0.50 | 111 | 7.6 | 15.5 | 58.0 |
| WB19 | 30.174 | 0.29 | 65.5 | 6.5 | 13.2 | 58.1 |
| WB20 | 29.753 | 0.34 | 76.3 | 8.2 | 14.2 | 50.3 |
| WB21 | 31.457 | 0.43 | 12.4 | 1.0 | 7.0 | 17.7 |
| WB22 | 30.360 | 0.41 | 74.7 | 6.6 | 13.0 | 54.1 |
| WB23 | 27.824 | 0.29 | 76.0 | 5.8 | N/A | N/A |
| WB24 | 27.439 | 0.22 | N/A | N/A | N/A | N/A |
| WB25 | 27.612 | 0.23 | 94.4 | 10.1 | 14.2 | 58.9 |
| WB26 | 27.710 | 0.28 | 105 | 8.6 | 15.5 | 59.7 |
| WB27 | 27.670 | 0.28 | 90.1 | 7.9 | 13.6 | 55.7 |

* All samples were collected between 13 and 15 Jul 99.
† Data in dpm per 100 liters.
‡ N/A, not available.

Table 2. Dissolved inorganic nitrogen (DIN) and radium isotopic data for Waquoit Bay groundwaters. Samples were collected along the head of Waquoit Bay between 13 and 15 Jul 99 by using drive-point piezometers. Additional samples ($n$=11) for DIN analysis only (GW4-15) were collected during Jul 00 and are presented as an average.

| Station | Salinity (ppt) | DIN ($\mu$M) | $^{224}$Ra* | $^{223}$Ra* | $^{226}$Ra* | $^{228}$Ra* |
|---|---|---|---|---|---|---|
| GW1 | 10.614 | 42.0 | 1290 | 99.5 | 159 | 674 |
| GW2 | 0.138 | 0.71 | 588 | 51.5 | 88.1 | 324 |
| GW3 | 4.588 | 116 | 538 | 23.9 | 24.2 | 95.4 |
| GW4-15 | | 59.3 ± 46.4 | | | | |

* Data in dpm per 100 liters.

*Estimating submarine groundwater discharge to Waquoit Bay from a 226-radium mass-balance*—In order to estimate submarine groundwater discharge, we first calculated the excess inventory of radium-226 (due to groundwater flux) in Waquoit Bay. This includes all sources of radium other than groundwater such as tidal exchange, rivers, and diffusion from the sediments. Expressed mathematically, the excess $^{226}$Ra ($^{226}$Ra$_{ex}$ [dpm d$^{-1}$]) in the bay equals

$$^{226}\mathrm{Ra}_{\mathrm{ex}} = \left[\frac{(^{226}\mathrm{Ra}_{\mathrm{WB}} - {}^{226}\mathrm{Ra}_{\mathrm{VS}}) \times V_{\mathrm{WB}}}{T_w}\right] - [^{226}\mathrm{Ra}_R \times F_R] - [^{226}\mathrm{Ra}_{\mathrm{SED}} \times A_{\mathrm{WB}}] \quad (2)$$

where $^{226}$Ra$_{WB}$ is the average activity in Waquoit Bay, $^{226}$Ra$_{VS}$ is the activity Vineyard Sound waters which exchange tidally with the bay, $^{226}$Ra$_R$ is the riverine activity, $F_R$ is the stream gauge flux of the rivers, $^{226}$Ra$_{SED}$ is the regeneration rate of desorbable radium in the sediments, $V_{WB}$ is the water volume of the study area, $A_{WB}$ is the surface area of the study area, and $T_w$ is the residence time calculated from equation (1) (Moore 1996).

The daily flux of $^{226}$Ra due to tidal exchange is a function of the flushing time of the estuary and the average $^{226}$Ra activities observed within the estuary. For this calculation, we used the average difference between Waquoit Bay and Vineyard Sound $^{226}$Ra (59 dpm m$^{-3}$), the average age of Waquoit Bay waters determined from $^{223}$Ra/ex$^{228}$Ra activity ratios (9.4 d) and a water volume of Waquoit Bay equal to 6.3 × 10$^6$ m$^3$ to calculate a daily $^{226}$Ra flux of 39 × 10$^6$ dpm d$^{-1}$.

The watersheds associated with the brackish rivers that discharge into Waquoit Bay are also a significant source of $^{226}$Ra to the system. We calculated the flux with $^{226}$Ra measurements taken at the mouths of the rivers during an ebbing tide and USGS stream-gauge data for the week of our experiment. Using a river discharge of 35,400 m$^3$ d$^{-1}$, the riverine $^{226}$Ra flux was 5.9 × 10$^6$ dpm d$^{-1}$, or ~15% of the total $^{226}$Ra flux from the bay. It is important to note that this flux calculation would include any SGWD-derived radium to the brackish Childs and Quashnet River estuaries; in this study, we are specifically interested in direct SGWD to Waquoit Bay proper. Also, we assume that any desorption of radium from river-borne suspended sediments has taken place upstream of our sampling station.

To demonstrate that diffusion from sediments contributes little to the $^{226}$Ra mass balance, we used a simple approach to estimate an upper-limit flux. Radium-226 is produced by radioactive decay of its parent nuclide, thorium-230. Therefore, it is generated at a fixed rate in the sediments based on its half-life. Also, only the fraction of $^{226}$Ra that is surface bound is available for exchange with saline porewater. We calculated a generation rate of 0.044 dpm m$^{-2}$ d$^{-1}$, which was based on the $^{230}$Th inventory from a local sediment core (0–10 cm) and the assumption that ~70% of the radium was available for desorption (Rama and Moore 1996). When normalized to the area of Waquoit Bay, this produced an upper-limit daily flux of 0.17 × 10$^6$ dpm d$^{-1}$, a minor fraction of the total $^{226}$Ra budget. Substituting these values into equation (2) gives an excess $^{226}$Ra flux of 33 × 10$^6$ dpm d$^{-1}$.

Having accounted for all possible sources of $^{226}$Ra, we assume that this excess activity from equation (2) is due to SGWD. Therefore, using measurements in wells adjacent to Waquoit Bay (Table 2), we calculated the groundwater flux (SGWD) from the equation

$$\mathrm{SGWD} = \frac{^{226}\mathrm{Ra}_{\mathrm{ex}}}{^{226}\mathrm{Ra}_{\mathrm{GW}}} \quad (3)$$

Table 3. Dissolved inorganic nitrogen (DIN) fluxes normalized to the surface area of each basin. New production values were calculated assuming the DIN is converted into biomass.

| Basin | DIN flux (kg yr$^{-1}$) | Area ($10^5$ m$^2$)* | Normalized DIN flux (mmol N m$^{-2}$ d$^{-1}$) | New production (mmol C m$^{-2}$ d$^{-1}$)† |
|---|---|---|---|---|
| Waquoit Bay SGWD | 11,000 | 39 | 0.55 | 3.7 |
| Quashnet River | 15,000‡ | 1.9 | 15 | 100 |
| Childs River | 14,000‡ | 1.5 | 19 | 120 |
| Sage Lot Pond | 330‡ | 1.5 | 0.43 | 2.9 |

* Cambareri and Eichner (1998).
† Assumming Redfield C : N ratio of 6.6.
‡ Estimates of Valiea et al. (1992).

where $^{226}Ra_{GW}$ is the average activity of $^{226}$Ra in the wells (Table 2). A $^{226}Ra_{GW}$ of 900 dpm m$^{-3}$ produces an average daily SGWD flux of ~37,000 m$^3$ d$^{-1}$.

The radium-derived groundwater flux is in close agreement with a recent estimate of 23,700–27,700 m$^3$ d$^{-1}$ based on rainfall recharge rates to the watershed (Cambareri and Eichner 1998). With a total freshwater recharge of 70,900–83,000 m$^3$ d$^{-1}$, SGWD constitutes more than one-third of the total freshwater budget for Waquoit Bay (Cambareri and Eichner 1998). To compare the magnitude of these fluxes, the largest freshwater springs in Florida discharge 241,000 m$^3$ d$^{-1}$ (Cable et al. 1997). In contrast, Moore (1996) used a similar radium-based approach to estimate a SGWD flux of $3 \times 10^6$ m$^3$ d$^{-1}$ to the South Atlantic Bight.

*Dissolved inorganic nitrogen flux to Waquoit Bay*—Urbanization has a twofold effect on DIN fluxes to coastal Cape Cod waters: (1) installation of private sewer systems increases DIN loading to the water table and (2) deforestation reduces the amount of precipitation-borne DIN that is intercepted by plant-life in the watershed (Valiela et al. 1992). Valiela and Costa (1988) estimated that <30% of anthropogenic DIN on Cape Cod was attenuated by the aquifer before entering receiving waters. They suggested that the attenuation rate was a function of the transit time from the wastewater source, rates of microbial processes (i.e., denitrification), and the form of DIN being transported (i.e., $NH_4^+$, which has an affinity for particle surfaces).

We estimated the DIN flux to Waquoit Bay using the radium-derived SGWD rate and the concentrations in the end-member well samples. In these groundwater samples taken from around Waquoit Bay, total DIN ($NO_3^-$ plus $NH_4^+$) concentration averaged 58 $\mu$M (Table 2). Using our calculated groundwater flux, this translates to a DIN flux of ~2100 mol N d$^{-1}$ (11,000 kg N yr$^{-1}$). Since we collected nutrient samples from drive-point well samples collected along the shoreline, our flux estimates are not dependent on chemical transformations that may take place during the transport of groundwater DIN to Waquoit Bay.

Our ability to provide an accurate estimate for the DIN flux is limited by the small number of groundwater end-member samples used in the calculation ($n = 15$). Valiela et al. (1992) collected hundreds of groundwater samples for three main subwatersheds within Waquoit Bay (Childs River, Quashnet River, and Sage Lot Pond). From their data, we calculated a weighted average DIN concentration of 35 $\mu$M; using this average value would reduce our estimate of DIN loading by approximately one third and highlights the importance of obtaining a significant and representative data set for calculating fluxes.

Normalized to the area of the estuary, our DIN flux estimate of 2100 mol N d$^{-1}$ becomes 0.55 mmol N m$^{-2}$ d$^{-1}$ (Table 3). Per unit area, the Childs River and Quashnet River subestuaries deliver nearly two orders of magnitude (19 and 15 mmol N m$^{-2}$ d$^{-1}$, respectively) more DIN than direct SGWD to Waquoit Bay. Assuming that this ''new'' DIN is utilized by plant biomass in the estuary, we converted the fluxes from Table 3 into carbon units using the Redfield C : N ratio of 6.6. These estimates of new production ranged from 3.7 mmol C m$^{-2}$ d$^{-1}$ for Waquoit Bay to 120 mmol C m$^{-2}$ d$^{-1}$ for the densely populated Childs River estuary.

Valiela et al. (1992) reported phytoplankton productivity rates, excluding macroalgae, ranging from 20 to 400 mmol C m$^{-3}$ d$^{-1}$ during the highly productive summer months. On the basis of the new production estimates from Table 3, we conclude that much of this productivity can be accounted for by DIN fluxes to Waquoit Bay from the Childs and Quashnet River subestuaries. Therefore, the delivery of DIN from SGWD to the subestuaries is likely as significant as direct SGWD to Waquoit Bay proper. These results highlight the importance of the subwatersheds (and their densely populated shorelines) versus direct groundwater discharge in the delivery of nutrients to Waquoit Bay.

As presented earlier, DIN concentrations in the bay were three orders of magnitude less than groundwater values during this study (July–August 1999). This lack of detectable DIN in the water column of Waquoit Bay is evidence that much of the nitrogen flux was converted to biomass and not exported to Vineyard Sound (as DIN) during the summer months. In contrast, winter productivity rates of <2 mmol C m$^{-3}$ d$^{-1}$ (Valiela et al., 1992) suggest that export of DIN to coastal waters may be significantly higher during colder months (under the assumption that SGWD remains fairly constant year-round).

*Conclusions*—We have applied radium isotopes in the study of nitrogen discharge from a coastal aquifer on Cape Cod where groundwater DIN levels were typically four orders of magnitude greater than those of the receiving waters. Although both DIN and radium were elevated in groundwater, the relative magnitude of enrichment was spatially variable over short distances. Our results indicate that the densely populated subwatersheds of Waquoit Bay deliver more DIN per unit area than direct SGWD to the estuary itself. Comparison of SGWD-derived fluxes of ''new'' nitrogen with published primary productivity estimates (Valiela et al. 1992) suggests that nitrogen is utilized during the summer but is likely exported to coastal waters during winter. On the basis of these results, future studies would be improved by adding time-series studies of DIN loading to Waquoit Bay, which includes sampling during all seasons. This would likely be accomplished through the use of remotely operated nutrient analyzers capable of high-frequency measurements.

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