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RADIUM-226 AS A TRACER OF GROUND WATER INPUT TO THE COASTAL WATERS OF SOUTHERN RHODE ISLAND

BY

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
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ABSTRACT

Submarine ground water discharge (SGWD) represents a significant, yet diffuse and largely neglected source of fresh water and dissolved constituents to the coastal environment. Quantification of this term therefore proves important with respect to coastal hydrological and geochemical mass balances. In order to better constrain SGWD to southern Rhode Island's coastal waters, the naturally-occurring radionuclide ^{226}Ra was used as a tracer of ground water input.

Activities of ^{226}Ra were determined in river water, salt ponds, coastal ocean and ground water in southern Rhode Island during the summer of 1997 (June-August). Coastal lagoons and shelf waters were analyzed to quantify excess radium inventories, signifying an input of ground water. Using these results, a radium box model was constructed from which the ground water flux to the salt ponds and/or shelf waters was calculated. For shelf waters off southern Rhode Island, ground water results appear unrealistic compared to river input to the region and watershed recharge estimates, implying that sources of ^{226}Ra in the ground water reservoirs of southern Rhode Island may not have been accounted for in this study. For the salt ponds, estimates of ground water flux are in most cases one order of magnitude less than inputs of river/stream water, with ground water inputs corresponding to ~1 to 42 x 10^5 L d^{-1}. Using these calculated ground water flows to the salt ponds, total inorganic N fluxes of ~0.3 to 15 kg N d^{-1} were determined based on local measurements of ground water nutrient concentration for Rhode Island's salt pond region.

ACKNOWLEDGMENT

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Finally, I would like to thank my friends and family for providing endless emotional support and inspiration in all aspects of my life. To my mother and father for always believing in me and molding me into the person I am today; and to my little brother, for providing breaks in my work time and always knowing the right thing to say to make me smile. Most of all, I thank the one closest to me (my B.F.B.F.) Kraig, for his love and encouragement, laughter and smiles, and big hugs at the end of a long day… without him, my life would be incomplete.

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Chapter 1

GENERAL INFORMATION

1.1 Rationale

Submarine ground water discharge (SGWD) is an important, yet poorly constrained source of fresh water and dissolved terrestrial material to coastal waters. Defined as the direct flow of water into the sea through sediments and porous rocks (Johannes, 1980; Figure 1.1), SGWD represents an important pathway of dissolved material, nutrients and pollutants to the coastal marine environment (Simmons, 1992; Valiela *et al.*, 1990; Lee and Olsen, 1985; Olsen and Lee, 1985). The concentrations of dissolved constituents in SGWD are often much higher than those of rivers, streams or coastal waters, characterizing SGWD with a distinct chemical signal (Church, 1996). Inputs of SGWD to the coastal zone can therefore affect the waters chemically, due to their significant carrying capacity of dissolved chemicals which bypass estuarine removal processes that modify river inputs. In addition, SGWD represents an important source of dissolved nutrients that can result in increased rates of biological productivity and hence affect the ecology of shelf waters (Weiskel and Howes, 1992; Valiela *et al.*, 1990; Lee and Olsen, 1985; Olsen and Lee, 1985)

The significance of ground water as a transport mechanism to the coastal environment has become increasingly apparent (Simmons, 1992; Weiskel and Howes, 1992; Valiela *et al.*, 1990; Lee and Olsen, 1985; Olsen and Lee, 1985; Bokuniewicz and Zeitlin, 1980), yet in

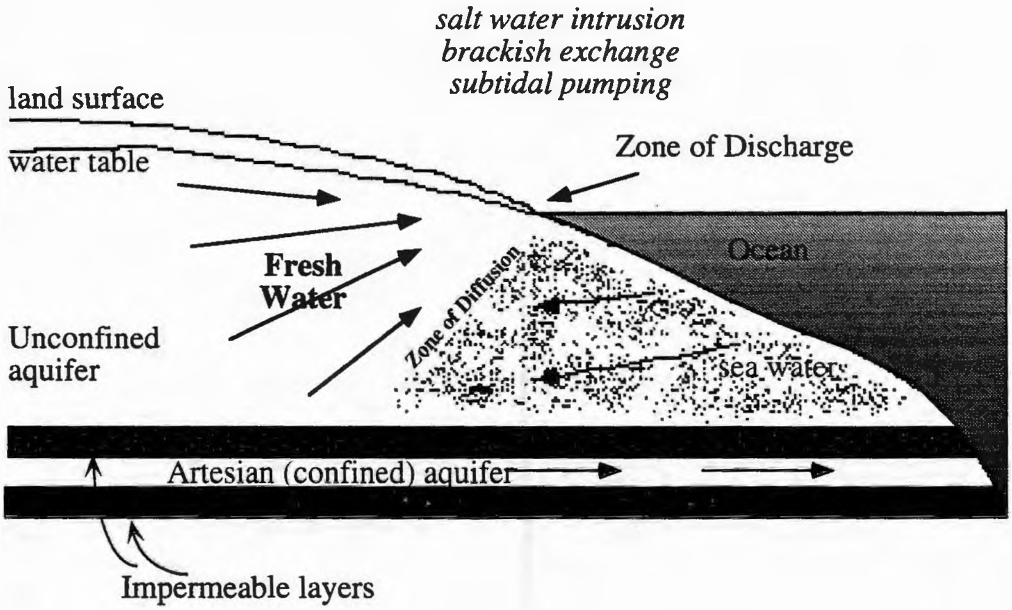


Figure 1.1 Schematic of idealized submarine ground water discharge (SGWD), adapted from Johannes (1980).

most mass balances, SGWD still remains a neglected source of fresh water and dissolved material to coastal ecosystems. Near-shore water budgets neglecting this input may be in error, especially in light of recent studies revealing large ground water sources to the coastal ocean. For example, Moore (1996) reported that the transport of SGWD to the South Atlantic Bight (SAB) and its soluble constituents may represent as much as 40% of the riverine input to this region. The implications of such findings are far-reaching, especially with respect to terrestrial fluxes of dissolved materials and the oceanic geochemical budget. Quantifying SGWD is therefore critical to developing accurate models of hydrology, biological productivity, nutrient cycling and the fate and transport of anthropogenic contaminants, such as organic contaminants and heavy metals, in the coastal environment.

1.2 Basis for Radium as a Ground Water Tracer

Previous approaches used to study ground water inputs to the coastal zone include *in-situ* measurements, seep meters and diffusion gradient models (Cable *et al.*, 1997; Buxton and Modica, 1992; Simmons, 1992; Bokuniewicz and Zeitlin, 1980; Lee, 1977). Although these methods yield evidence for the existence of ground water movement, they provide only limited information on ground water flux, due primarily to the large-scale and diffuse nature of SGWD. Quantification of the magnitude of SGWD on a regional scale is needed to accurately assess its impact on the coastal marine ocean.

The naturally-occurring radium isotopes, ^{226}Ra, ^{228}Ra, ^{224}Ra and ^{223}Ra, have been recently used as tracers to quantify SGWD to the coastal zone (Moore, 1997, 1996; Rama and Moore, 1996). A key advantage of the radionuclide tracer approach, specifically using the mentioned radium isotopes of the ^{238}U, ^{232}Th and ^{235}U decay series, is that due to their known production and decay rates (Figure 1.2), these tracers are useful chronometers for determining the rates of processes. In riverine systems, radium is strongly adsorbed to particles, whereas in seawater, it is primarily dissolved (Moore and Todd, 1993). With respect to coastal waters, sources of radium include erosion of terrestrial sediments, river water, desorption from river sediments/particles, exchange with open ocean and ground water input (Moore, 1996; Elsinger and Moore, 1983). The applicability of radium as a tracer of ground water input to shelf waters (Moore, 1997, 1996) and salt marshes (Rama and Moore, 1996) has been recently examined. Findings from these studies suggest that the two primary reasons why radium, particularly ^{226}Ra, can be used to study SGWD are: (1) its enrichment in coastal waters, and; (2) its activity in ground water.

1.2.1 Coastal Enrichment

Moore (1996) reported ^{226}Ra activities (average ~19 dpm 100 L^{-1}) in the inner shelf waters of the SAB, which were elevated compared to open ocean values of ~8 dpm 100 L^{-1}. Moore (1996) determined that riverine sources to the SAB could only support approximately 5% of the required excess, and that the observed coastal enrichments were the result of ground water input to the inner shelf region. Additional evidence of coastal-zone enrichment of ^{226}Ra in the North Inlet salt marsh was also reported by Rama and

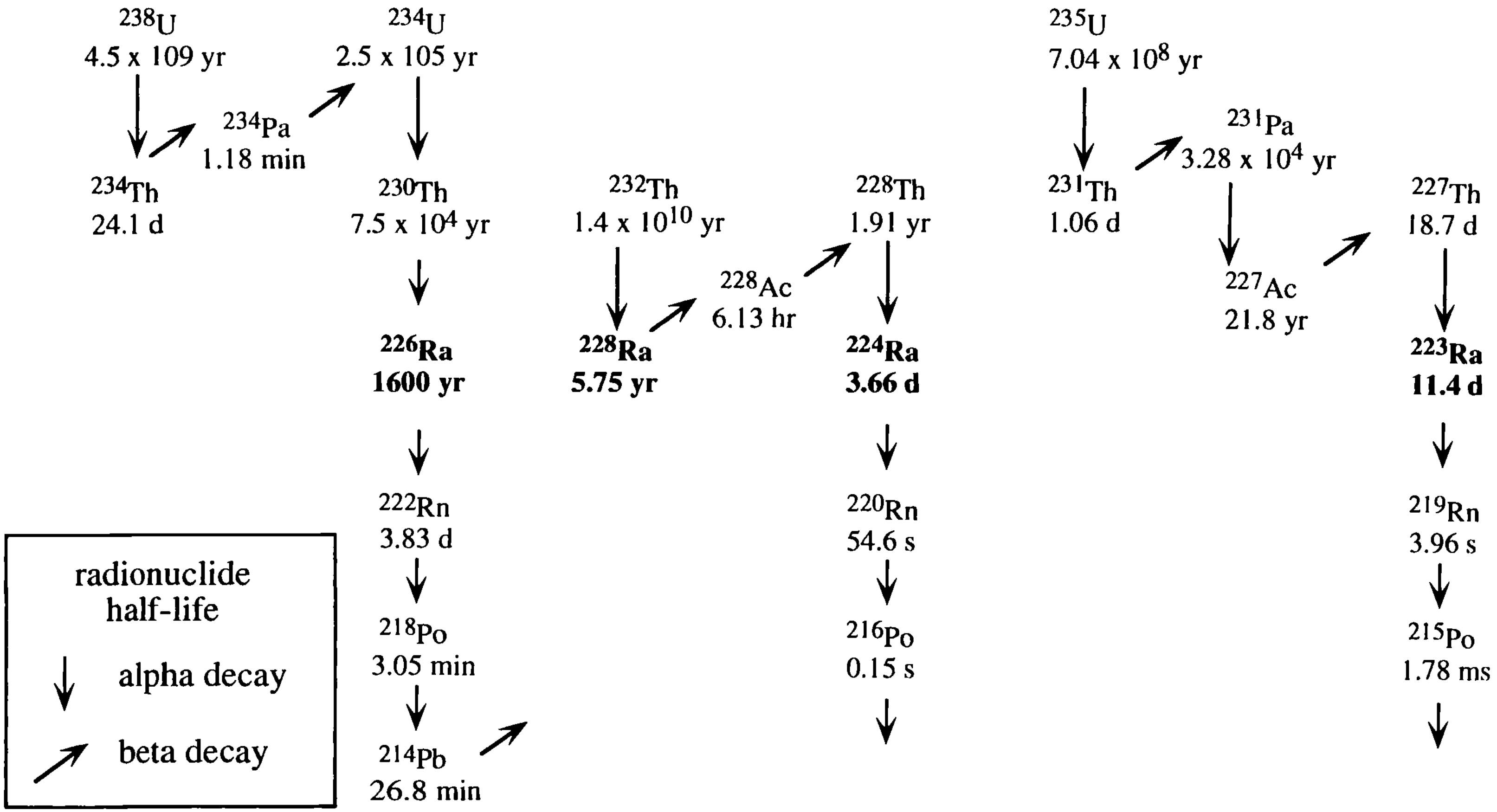


Figure 1.2 Chart indicating radium isotopes used to study ground water of the ^{238}U, ^{232}Th and ^{235}U decay series.

Moore (1996), in which salt marsh water samples clearly indicated elevated levels of ^{226}Ra, averaging ~22 dpm 100 L^{-1}. The excess ^{226}Ra in the salt marsh was determined to be contributed only from ground water sources, as generation in surface sediments, pore water diffusion and sediment influx were negligible.

1.2.2 Radium Activity in Ground Water

With respect to activity, radium levels have been found to be significantly greater in ground water than in river water and coastal water. For example, brackish ground waters from the North Inlet Marsh in the SAB were characterized by ^{226}Ra activities on the order of 100-800 dpm 100 L^{-1} (Moore, 1996). These values are approximately 10-100 times average open ocean ^{226}Ra activities. For many geographic areas, contact with granitic bedrock provides an excellent source of radium for ground water as it flows towards coastal areas, resulting in enriched ^{226}Ra activities. In cases of highly elevated ground water, however, salt water intrusion has been suggested to be responsible for heightened ^{226}Ra activities (Moore, 1996). As salt water invades a coastal aquifer and comes into contact with fresh water, ^{226}Ra is desorbed from suspended particles, resulting in increased ground water ^{226}Ra activities. In either instance, these high ^{226}Ra levels, in comparison to river water and ocean water, inherently make radium a useful tracer of ground water.

1.3 Scientific Approach: Radium Balance

The basic strategy for evaluating SGWD to coastal waters using isotopes of radium as tracers has been extensively described in papers by Moore (1997, 1996) and Rama and Moore (1996). In this approach, ground water fluxes are calculated by constructing a radium box model, in which radium activities are determined for each of the following component variables: river water, coastal lagoon, coastal ocean, open ocean and ground water (Figure 1.3). Depending upon the scope of the study area involved (i.e. shelf waters vs. coastal lagoons), slight modifications are reflected in the overall radium mass balance. The key principle of the approach, however, is not altered; radium enrichments (measured activities minus ocean activity) for the shelf waters and/or coastal lagoons, when calculated as a net offshore flux by considering rates of water exchange, must balance the input of radium from riverine and ground water sources (Moore, 1997, 1996; Rama and Moore, 1996). It is important to note that an assumption made in this approach is that an enrichment of radium in the coastal waters is encountered; otherwise, this technique is not applicable as a method for examining ground water in the coastal zone.

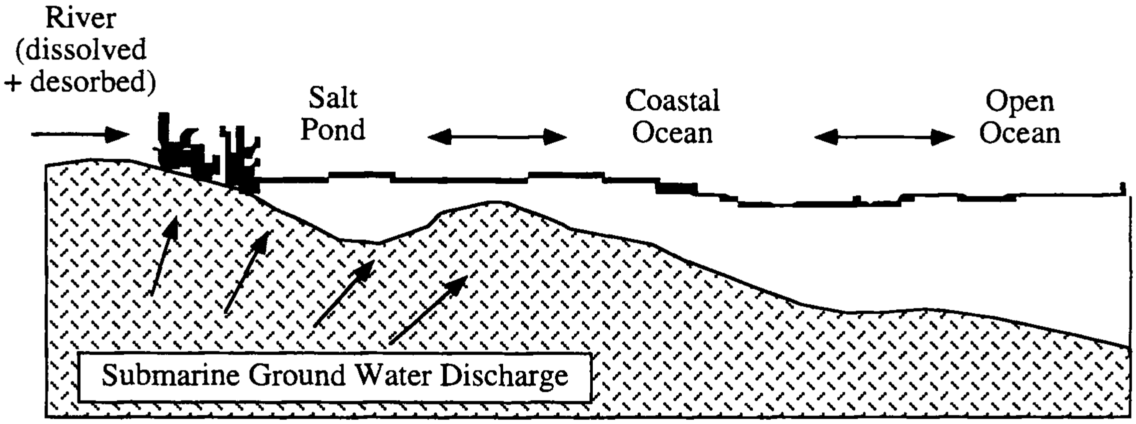


Figure 1.3 Components involved in radium box model used in this study.

1.4 Objectives and Organization of Thesis

The overall goal of this study is to investigate the use of radium, specifically ^{226}Ra, as a ground water tracer in the coastal environment. The specific objectives are:

1.) to quantify the magnitude of SGWD to the coastal ponds of southern Rhode Island and adjacent shelf waters, and;

2.) to aid in determining the relative importance of ground water as a component of coastal-zone fresh water input.

Details of the methods used for collection and analysis of samples are outlined in Chapter 2. An explicit description of the equations used to determine ground water flux to the shelf waters and salt ponds, as well as the methods used to determine ^{226}Ra activity (gamma spectrometry and ^{222}Rn-emanation), are also given in this chapter.

Chapter 3 presents ground water flux results for the salt ponds of southern Rhode Island and adjacent shelf waters. For both shelf water and salt pond ground water inputs, a comparison to fresh water from riverine sources is made. Estimated recharge for the watershed area of southern Rhode Island, serving as a check for ground water input to the shelf region, are calculated. Previous ground water studies for the salt ponds of southern Rhode Island are compared and discussed. The salt pond variables of pore water ^{226}Ra activity, tidal range and residence time, and their impact upon ground water flux calculations as determined by the given equations, are examined. Nutrient concentrations from salt pond and ground water samples, and their potential for calculating nutrient influx to the salt ponds, as well as serving as a ground water source identifier, are also discussed in Chapter 4.

Chapter 4 summarizes the principle conclusions and implications of this study for the coastal waters of southern Rhode Island, outlining areas of future research concerning radium isotopes as ground water tracers.

In addition to the main chapters, section D of the Appendix presents radium distributions (^{226}Ra, ^{228}Ra) and initial ground water flux results for the shelf waters of the Gulf of Maine and Scotian Shelf. River inputs to the region for the duration of study (September 1997) are compared to the calculated ground water inflows. A discussion of the measured ^{226}Ra activities and their relationship to sampling techniques is also provided.

Chapter 2

METHODS AND MATERIALS

2.1 Introduction

This chapter describes the methods and materials implemented for the collection and analysis of ^{226}Ra water activities in coastal water and ground water. For this ground water study, the coastal lagoons of southern Rhode Island and adjacent shelf waters were examined. Details of the study area, sampling sites and ground water flux results are presented in Chapter 3. Methodology concerning the ancillary measurements of salinity, nutrient content and organic carbon (POC and TOC) is also described in Chapter 2, with results given in the subsequent chapter.

2.2 Radium Balance: Background and Theory

2.2.1 Shelf Waters

For the off-shore Rhode Island regions, ^{226}Ra tracer distributions were determined in the shelf waters, open ocean, ground water and contributing rivers. Activities in the shelf waters and open ocean were obtained from surface (less than 3 m depth) seawater samples. Ground water activities were measured from ground water well samples located along the coast of southern Rhode Island. The ^{226}Ra contribution from river supply (dissolved and desorbed) was not determined directly. Rather it was estimated from previous radium studies along the Eastern U.S. region (Moore, 1996; Elsinger and Moore, 1983, 1980; Li and Chan, 1979; Li *et al.*, 1977) and from U.S. Geological Survey data; specifically, using river discharge rates and suspended sediment loadings. The activity of ^{226}Ra supported by rivers is calculated using the following equation:

$$^{226}\mathrm{Ra}_{river} = \frac{(^{226}\mathrm{Ra}_{total} \times \tau)}{\mathrm{V}_{shelf}} \tag{2.1}$$

where $^{226}\mathrm{Ra}_{river}$ is riverine supported activity (dpm 100 L^{-1}), $^{226}\mathrm{Ra}_{total}$ is total river input (dpm d^{-1}), τ is the residence time of the ^{226}Ra-enriched shelf waters (d), and V_{shelf} is the volume of shelf waters enriched in ^{226}Ra (L).

By comparing the above ^{226}Ra contribution due to river input with the average ^{226}Ra enrichment in the coastal zone, an estimate can be made as to whether SGWD may be responsible for the observed radium enrichments. Specifically, the amount of ground water required to balance the excess in ^{226}Ra can be calculated as follows:

$$\mathrm{G}_f = \frac{(^{226}\mathrm{Ra}_{ex} \times \mathrm{V}_{shelf})}{(^{226}\mathrm{Ra}_{GW} \times \tau)} \tag{2.2}$$

where G_f is the determined ground water flux (L d^{-1}), $^{226}\mathrm{Ra}_{ex}$ is the required excess ^{226}Ra input (dpm 100 L^{-1}) (defined as the average activity of the enriched shelf waters minus activity due to desorption in estuaries minus open ocean activity), and $^{226}Ra_{GW}$ is the ground water ^{226}Ra activity (dpm 100 L^{-1}).

2.2.2 Coastal Lagoons

For the coastal ponds along the southern shore of Rhode Island (referred to as "salt ponds"), a modified approach for determining SGWD must be taken. In addition to the local ground water activities, ^{226}Ra tracer distributions must be determined in the salt ponds and sediment pore waters. Using the ^{226}Ra budget, the ground water flux can then be estimated to each of the Rhode Island salt ponds. This approach is essentially the same as that used by Rama and Moore (1996) in their study of water exchange in the North Inlet salt marsh.

As in the case of the Rhode Island shelf waters, the total excess ^{226}Ra must be determined for the salt pond in question. This contribution, $^{226}Ra_{ex}$, is the difference between the average ^{226}Ra activity in the salt pond and the concentration in the pond's respective inlet (i.e. breachway) at high tide. Since every salt pond in this study does not necessarily have a permanent inlet and the breachways were not always sampled at high tide, the average ^{226}Ra activity in the coastal shelf waters entering the ponds will replace the inlet term in determining $^{226}Ra_{ex}$. The $^{226}Ra_{ex}$ flux, $^{226}Ra_{ex,F}$, from the salt pond is calculated using the following equation:

$$^{226}\mathrm{Ra}_{ex,F} = \frac{(^{226}\mathrm{Ra}_{ex} \times \mathrm{H})}{\tau_{SP}} \qquad (2.3)$$

where $^{226}\mathrm{Ra}_{ex,F}$ is the total ^{226}Ra export flux (dpm cm^{-2} d^{-1}), $^{226}\mathrm{Ra}_{ex}$ represents excess ^{226}Ra (dpm 100 L^{-1}) (calculated as the average salt pond activity minus open ocean activity), H is the tidal range of the salt pond (cm), and τ_{SP} is the residence time of the salt pond (d).

In the absence of ground water, the total export flux of ^{226}Ra from the salt pond or marsh should be balanced by inputs of ^{226}Ra from streams, marsh sediments and sediment pore waters (i.e. $^{226}\mathrm{Ra}_{influx}$). Differences between these two terms suggests advection of ground water into the system. The salt ponds of southern Rhode Island do not receive any significant inputs of fresh water from creeks, streams or fresh springs (Ely, 1990; Lee and Olsen, 1985), and data that do exist for fresh water inputs are limited (Ernst, 1996). When stream data are available, the $^{226}\mathrm{Ra}_{ex}$ term is corrected for stream contribution (dissolved and desorbed). For salt ponds where stream data may be lacking, only the pore water (here, representative of ground water) and sediment terms are considered in determining the input flux of ^{226}Ra. In addition, due to the sandy nature of the salt pond sediments, the pore water diffusive influx can be eliminated. Sediment-supported ^{226}Ra activities are determined from the top ~5 cm of sediment. Desorbable contributions from sediments below 5 cm are assumed to be negligible due to the slow rate of ^{226}Ra regeneration (Rama and Moore, 1996).

Thus, the ground water calculation is simplified to that difference between the excess ^{226}Ra export flux and total influx terms, balanced by ^{226}Ra pore water activity, expressed in the following equation:

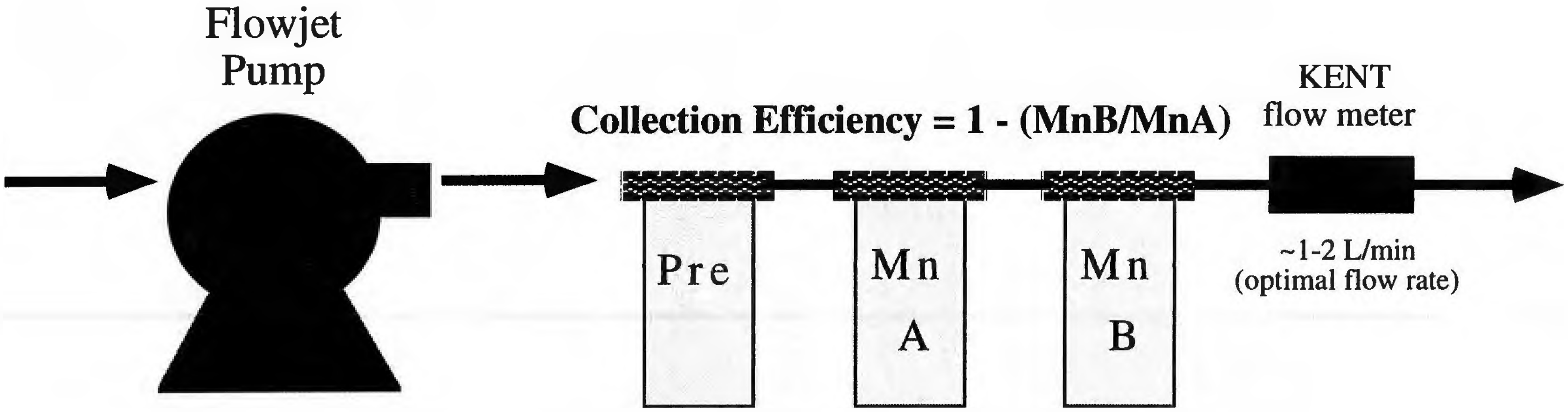
$$G_f = \frac{^{226}Ra_{ex,F} - {}^{226}Ra_{influx}}{^{226}Ra_{PW}} \qquad (2.4)$$

where G_f is the calculated ground water flux (cm^3 cm^{-2} d^{-1} or mL cm^{-2} d^{-1}), $^{226}Ra_{ex,F}$ represents the total ^{226}Ra export flux (dpm cm^{-2} d^{-1}), $^{226}Ra_{influx}$ is the total ^{226}Ra influx or the sum of the contributions from streams, sediment-supported ^{226}Ra, pore water diffusion and sediment influx (dpm cm^{-2} d^{-1}), and $^{226}Ra_{PW}$ is the activity of the sediment pore water (dpm cm^{-3} or dpm mL^{-1}).

2.3 Sample Collection

2.3.1 Large-Volume Sampling

Surface water samples (from less than 3 meters depth) were collected from both shelf water and coastal lagoons, with slight modifications in sample collection made for each site. ***In-situ*** surface water samples were pumped through cartridges of the in-line sampling assemblage illustrated in Figure 2.1. Suspended particles were initially removed by filtering through a 10-inch, 1 μm nominal pore size polypropylene (Hydrex II) prefilter. Dissolved ^{226}Ra was collected on two 3.3-inch MnO_2 impregnated absorber



- 3/4" fittings on cartridge holders
- 1 um prefilter; 10" long
- 5 um Mn-A and Mn-B; 3.3 " long

Figure 2.1 Schematic illustrating the in-line pumping assemblage for large-volume water sampling.

cartridges connected in-series. The collection time and sample volume were recorded. Sample volumes ranged from 50 to 1000 L, with flow rates between 1-10 L min^{-1}. In most cases, water samples were collected at an optimal flow rate of 1-2 L min^{-1}. It has been observed that sampling at these lower flow rates ensures efficient radium adsorption onto the absorber cartridges (Figure 2.2). Flow rates were determined through the use of an in-line Kent flow meter, calibrated in the laboratory prior to sampling. Collection efficiencies were determined from the in-series design of the cartridge sampling assembly, using the equation:

$$\text{Collection Efficiency} = 1 - \frac{\text{MnB}}{\text{MnA}} \qquad (2.5)$$

where MnA and MnB refer to the sample counts per minute (cpm) determined for each of the two MnO_2 adsorber cartridges (also, see 2.4 Analysis).

2.3.2 Sediment Cores

Sediment cores were collected from each of the salt ponds studied in order to determine the pore water radium contribution and sediment-supported ^{226}Ra activity. Cores were obtained using a push-core apparatus composed of butyrate, approximately 0.5 m in length with 2-7/8-inch inner diameter and 3-inch outer diameter dimensions. After extracting the sediment, the core ends were sealed with electrical tape to prevent leakage and maintain the distribution of pore water within the sediment. In the laboratory, water

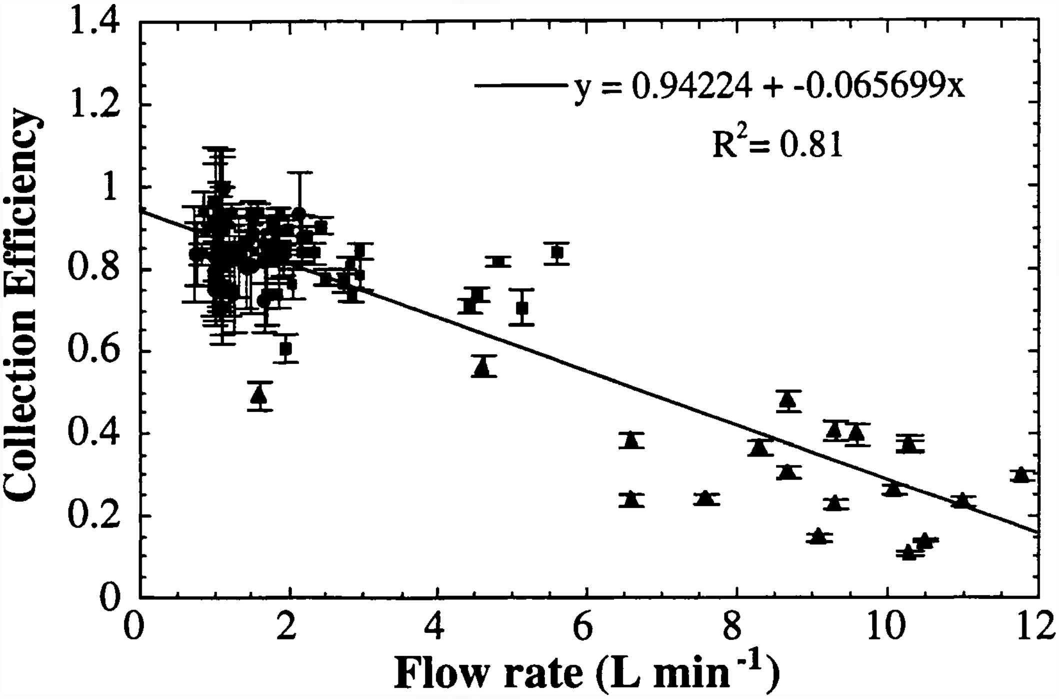


Figure 2.2 Collection efficiency of ^{226}Ra on MnO_2 cartridges. Samples from southern Rhode Island (● - 1997); the Gulf of Maine and Scotian Shelf region (▲ - 1997), and; Arctic Ocean (▪ - B. Moran, unpublished data).

above the sediment interface was siphoned off and stored in 500 mL Nalgene bottles. Sediment cores were sectioned at approximately 5 cm intervals and placed in acid-leached 500 mL Nalgene centrifuge bottles and the sample mass recorded (g, wet weight). Using a Sorvall RC-5B Refrigerated Superspeed centrifuge, samples were centrifuged at 8000 rpm for approximately 30 minutes. Pore water was poured into 2 L glass vessels used for ^{222}Rn-emanation analysis, with a record made of the pore water sample weight and volume. After centrifuging, sediment samples were transferred to 500 mL Nalgene bottles and refrigerated (~5°C).

2.4 Analyses

2.4.1 Gamma Spectrometry

Analysis of dissolved ^{226}Ra on the two MnO_2 adsorber cartridges was conducted by gamma spectrometry. A high efficiency germanium well detector was employed for determining ^{226}Ra activities.

2.4.1.a Gamma Spectrometry: Sample Preparation and Counting

After the large-volume water samples were collected, the filter cartridges were dried overnight (90°C) and subsequently ashed in a muffle furnace at 575°C for approximately 8 hours. The ash from each filter cartridge was weighed, with the mass recorded, and then blended to a constant consistency using a spatula. The resulting homogenized ash was packed in polystyrene counting vials (1.5 cm diameter, 3.75 cm length) to a constant density (0.875 g mL^{-1}) and sealed with epoxy. Both the mass and ash volume (i.e. the height of the sample in the counting tube) were recorded. An ingrowth period of at least two weeks was allowed for ^{222}Rn and its alpha daughters, ^{218}Po and ^{214}Pb, to approach secular equilibrium[1] with ^{226}Ra. Samples were then gamma counted for ^{226}Ra (via ^{214}Pb at 351.9 keV) to a precision of 5-15% (1σ). Note that direct determination of ^{226}Ra from its 186 keV peak was not employed, as a distinct energy peak could not be ascertained due to overlapping contributions from adjacent radionuclides. For each sample, net cpm was converted to dpm by the following equation:

$$\text{dpm} = \frac{\text{cpm}}{E \times B \times A} \qquad (2.6)$$

where E is the detector efficiency evaluated using the plot of Figure 2.3, B is the branching ratio for ^{214}Pb (0.358), and A is the ash fraction (i.e. amount of counted ash compared to total sample ash) (Moore, 1984). Collection efficiency and volume of sample pumped were further considered for calculating dpm 100 L^{-1} values. No

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[1] Secular equilibrium is defined as a state of radioactive equilibrium where the decay rate of the parent (λ_1) is much less than the decay rate of the daughter isotope (λ_2) (i.e. $\lambda_1 << \lambda_2$) and the number of parent atoms is nearly constant over several daughter half-lives (i.e. the rate of decay of daughter is equal to the decay rate of parent) (Friedlander *et al.*, 1981).

corrections were made for MnO_2 ash absorbence at the 351.9 keV peak or for sample density.

2.4.1.b Gamma Spectrometry: Detector Calibration, Background Determinations and Ash Blanks

Energy calibration curves for varying ash volumes (2-6 mL) over a range of energy peaks (46.5 keV to 1333.2 keV) were determined using a mixed gamma standard (Appendix A), as a NIST ^{226}Ra standard was not available. From these plots, a standard efficiency curve for varying MnO_2 ash was calculated for ^{226}Ra (Figure 2.3), which was used to correct sample counts (see Equation 2.6). Efficiency uncertainties were based on counting error at 1σ.

Detector background corrections were performed automatically through the GENIE-PC counting software used by the well detector. In this program, the detector background under the curve is automatically subtracted from the total integrated peak area. The resulting integrated area, representative of sample counts corrected for background, is that which is reported.

In the case of relatively fresh water samples (i.e. ground water wells), blank considerations were necessary. These low salinity samples contained ash amounts at levels far below the normal 3.5 g (4 mL) sample mass, with average ash weights less than 0.2 g. For this reason, blank ash was mixed in to build up the sample ash to the stated

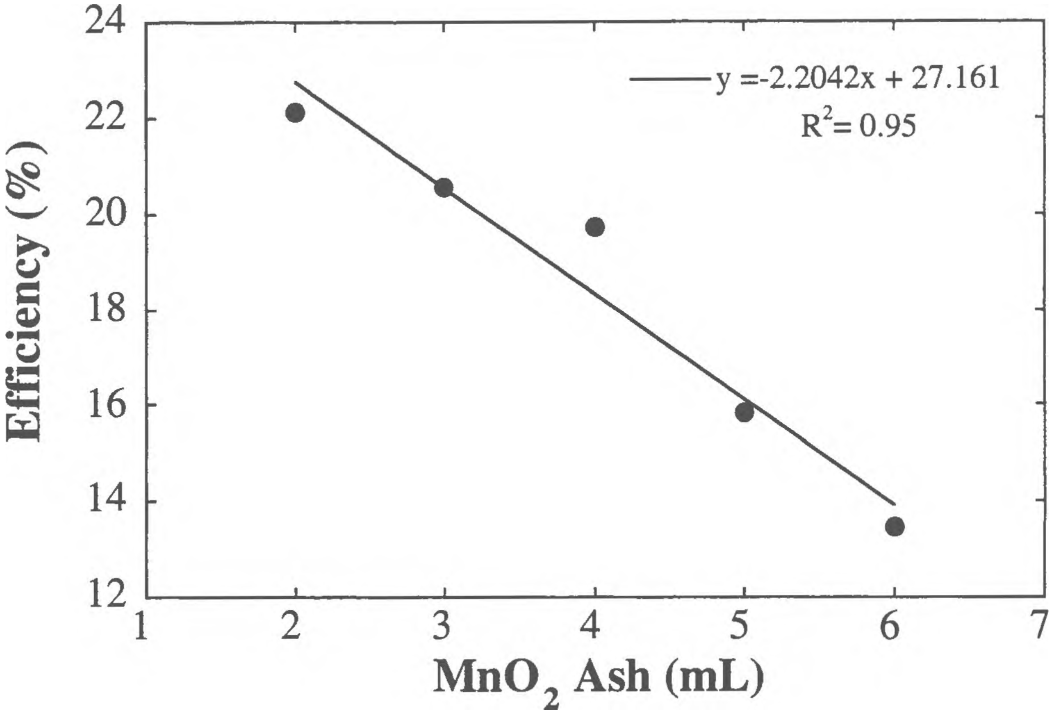

Figure 2.3 Efficiency of well detector for ^{226}Ra plotted against volume of MnO_2 ash. ^{226}Ra efficiencies were determined by counting ^{214}Pb at 351.9 keV.

Table 2.1 ^{226}Ra activities of ash blanks used for low salinity samples.

Ash Blank	^{226}Ra Activity ($^{+}$cpm)	*Sample
MBLD	0.048 ± 0.016	W3bA,B
MBLE	0.048 ± 0.017	W3aA,B
MBLF	0.038 ± 0.016	W2A,B
MBLH	0.030 ± 0.018	W1A,B
MBLI	0.061 ± 0.012	W5A,B
MBLJ	0.060 ± 0.017	W6A
MBLK	0.056 ± 0.018	W6B, SP7B
MBLL	0.070 ± 0.018	W7A
MBLM	0.077 ± 0.018	W8A,B
MBLQ	0.057 ± 0.017	W7B, SP7A

$^{+}$ Sample count per minute (cpm).

* Refers to low ash sample to which ash blank was added.

density requirement (0.875 g mL^{-1}). Ash blanks were derived from MnO_2 cartridges that had been exposed to ~20 L of "stripped" seawater[2]. The "blank" cartridges were then ashed, packed, sealed with epoxy, and held for two weeks before gamma counting. Those blank ash samples whose counts per minute (cpm) values were 1-2 orders of magnitude below "normal" ^{226}Ra samples (i.e. ~0.5-1 cpm) were used (Table 2.1). Corrections accounting for blank ash were made to each ground water well sample, accordingly.

2.4.2 ^{222}Rn-Emanation Line

^{226}Ra activities were also determined by ^{222}Rn-emanation, using a dual radon counting system and method described by Mathieu *et al.* (1988). This technique was used in this study primarily for small-volume samples (i.e. pore waters) and for determining sediment-supported ^{226}Ra activities. In addition, this method served as a means of validating ^{226}Ra results obtained by gamma spectrometry. A comparison of ^{226}Ra results obtained by gamma spectrometry and ^{222}Rn-emanation is discussed in Section 2.4.3.

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[2] "Stripped" seawater refers to seawater that had been initially cycled multiple times through the large-volume sampling setup, equipped with three 10-inch MnO_2 adsorber cartridges. The successive passing (2-3 cycles) of the seawater through the adsorber cartridges, in theory, "strips" the dissolved ^{226}Ra from the water.

2.4.2.a ^{222}Rn-line: Sample Preparation

For radon analysis, 2 L air-tight, glass vessels were employed. Small-volume pore water samples were brought up to an acceptable volume for analysis (~300-400 mL) using deionized water. Large-volume samples collected on MnO_2 impregnated filter cartridges were prepared by digesting approximately 0.5 g of ash in 8 N HNO_3 and drying to evaporation. Approximately 50 ml of 1.5 N HCl were then added to the evaporated ash residue, and the sample was again dried to evaporation. This step was repeated twice to ensure that no HNO_3 remained after digestion. After rinsing the beaker with 1.5 N HCl to put the dried digested ash back into solution, the resulting liquid was transferred into a 2 L glass radon extraction vessel and brought up to ~300-400 mL with 1.5 N HCl. For sediment samples, approximately 0.25 g of sediment was first oxidized with a 1:1 solution of concentrated HNO_3 and hydrogen peroxide (Hameed *et al.*, 1997) and dried to evaporation. The oxidized sediment was then digested and transferred to a 2 L radon vessel following the same steps outlined above for ash samples. After preparation, all samples were purged with helium for approximately 30 minutes, which drives off existing ^{222}Rn. Samples were then held for two weeks to attain secular equilibrium, after which ^{226}Ra activities were determined via ^{222}Rn extraction and transferred to scintillation cells for alpha counting.

2.4.2.b ^{222}Rn-line: Extraction System

A detailed schematic of the ^{222}Rn-line extraction system is provided in Figure 2.4. Helium was used as the carrier gas for the system, circulated by means of a vacuum/pressure pump. A column of dessicant (1/3 ascarite, 2/3 drierite, by volume) was used to remove CO_2 and water vapor from the circulating helium gas. From each of the prepared samples, the ingrown ^{222}Rn was extracted onto charcoal columns. The charcoal columns were placed in a Dewar container, which was filled with a cooling bath consisting of a mixture of dry ice and iso-propanol (-78°C). A bath temperature of -60°C is required for extracting ^{222}Rn from water samples (Mathieu *et al.*, 1988). To conserve space and increase sample throughput, two extraction systems were set up with the charcoal columns from each system sharing one cooling bath. An extraction time of 30 minutes was followed for each of the samples, with two samples processed per run.

2.4.2.c ^{222}Rn-line Transfer System and Scintillation Cells

Figure 2.4 also illustrates the transfer system used in the ^{222}Rn-emanation line. After extraction, each charcoal column was heated at 470°C in a temperature-controlled, heated glove for approximately 5 minutes. The trapped ^{222}Rn gas released from the column was transferred into the scintillation cell. Each scintillation cell is composed of a cylindrical quartz flask, chosen for its low ^{226}Ra content (Mathieu *et al.*, 1988). A thin conducting layer of tin oxide, overlaid with activated zinc sulfide, coats the inside of the flask. Layers of reflective white paint and protective electrical tape provide a covering for the outside

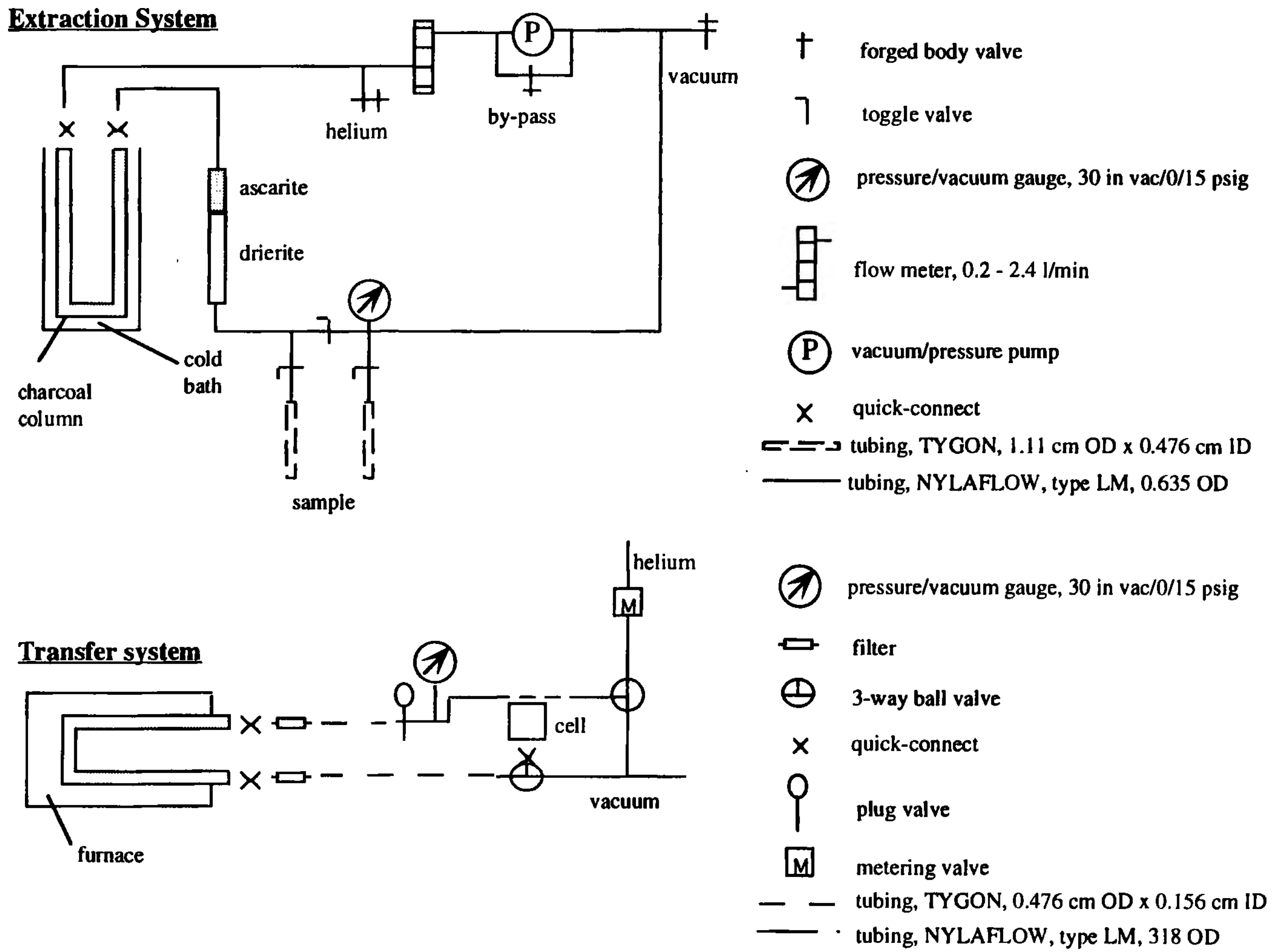

Figure 2.4 Diagram detailing the extraction and transfer systems of the ^{222}Rn-emanation line (adapted from Mathieu *et al.*, 1988).

of the cell. After transferring the ^{222}Rn gas into the scintillation cells, the samples were allowed to equilibrate for approximately three hours to allow the alpha daughters, ^{218}Po and ^{214}Pb, to approach secular equilibrium with ^{222}Rn. Samples were then duplicate counted on a dual Lucas cell radon counting system for approximately 18 and 6 hours, respectively. Note that consistency was strictly adhered to with respect to pairing of columns, scintillation cells and extraction systems (i.e. odd numbered columns were always run on extraction system A and transferred into odd numbered cells, while even numbered columns and cells were associated with extraction system B).

2.4.2.d ^{222}Rn-line Calibration, Blanks and Cell Backgrounds

Prepared liquid radium standards and procedural blanks were run weekly to ensure system efficiency and to correct for background. As with charcoal columns and scintillation cells, standards and blanks were also designated for specific extraction system usage (i.e. odd numbered standards and blanks were run on extraction system A; even numbered on system B).

All ^{226}Ra standards were derived from a primary NIST ^{226}Ra standard SRM 4967 (163,740 dpm g^{-1}). Dilute tertiary radium standards (~0.5 mL volume, ranging from 26.66-31.92 dpm g^{-1}) were created from a stock solution of working secondary standard (54.4 dpm g^{-1}) and brought up to an acceptable volume for analysis (~300-400 mL) with 1.5 N HCl. Cell efficiencies were similar for both transfer systems and alpha counters,

Table 2.2 Cell counter efficiencies for ^{222}Rn-emanation technique. Running averages are indicated in *italic*.

1(1)	1(2)	2(1)	2(2)	3(1)	3(2)
0.85	0.89	0.83	0.84	0.82	0.86
0.83	0.83	0.81	0.84	0.92	0.91
0.78	0.86	0.84	0.87	0.90	0.90
0.89	0.87	0.86	0.82	0.88	0.90
0.86	0.87	0.87	0.87	0.88	0.89
0.86	0.87	0.86	0.88		
0.87	0.88	0.87	0.88		
0.92	0.92	0.90	0.91		
0.90	0.91	0.90	0.90		
0.86	*0.88*	*0.86*	*0.87*	*0.88*	*0.89*

4(1)	4(2)	5(1)	5(2)	6(1)	6(2)
0.80	0.85	0.91	0.88	0.87	0.88
0.83	0.87	0.84	0.83	0.78	0.82
0.88	0.87	0.80	0.82	0.80	0.81
0.89	0.90	0.82	0.87	0.89	0.8
0.88	0.90	0.87	0.87	0.85	0.84
0.89	0.89	0.88	0.85	0.89	0.86
		0.89	0.91	0.91	0.88
		0.88			0.88
0.86	*0.88*	*0.86*	*0.86*	*0.86*	*0.85*

Note: Given notation, "cell#(counter)", refers to scintillation cell (ranging from 1-6), analyzed on counter (1 or 2). For example, "1(1)" translates to cell #1, analyzed on counter #1.

Table 2.3 Procedural blanks for ^{222}Rn-emanation technique.

Blank for Extraction System A *(cpm)	Date Effective	Blank for Extraction System B *(cpm)
0.889 ± 0.089	1/28/98	0.437 ± 0.044
0.639 ± 0.064	2/4/98	0.407 ± 0.041
0.728 ± 0.073	2/19/98	0.393 ± 0.039
0.728 ± 0.073	3/5/98	0.398 ± 0.040
0.886 ± 0.089	3/17/98	0.431 ± 0.043
0.783 ± 0.078	4/2/98	0.432 ± 0.043
1.007 ± 0.101	4/24/98	0.458 ± 0.046
0.539 ± 0.054	5/8/98	0.443 ±0.044
0.602 ± 0.060	5/20/98	0.444 ± 0.044
		0.427 ± 0.043

* cpm = counts per minute

Table 2.4 Cell backgrounds (in cpm) for ^{222}Rn-emanation technique. Running averages are indicated in *italic*.

1(1)	1(2)	2(1)	2(2)	3(1)	3(2)
0.34	0.41	0.29	0.15	0.29	0.14
0.31	0.15	0.30	0.15	1.0	0.58
0.55	0.29	0.35	0.22	0.37	0.20
0.42	0.25	0.41	0.21	0.45	0.22
0.47	0.33	0.35	0.43	0.51	0.23
0.32	0.25	0.31	0.23	0.33	0.37
0.33	0.25	0.31	0.23		0.30
0.39	*0.28*	*0.33*	*0.23*	*0.49*	*0.29*

4(1)	4(2)	5(1)	5(2)	6(1)	6(2)
0.88	0.15	0.32	0.18	0.35	0.17
0.47	0.97	0.37	0.15	0.32	0.15
0.33	0.19	0.36	0.19	0.38	0.19
0.43	0.23	0.21	0.21	0.32	0.31
0.22	0.22	0.33	0.27	0.33	0.23
0.45	0.22	0.38	0.20	0.33	0.21
0.31	0.36	0.35	0.24	0.33	0.26
	0.25		0.25		0.26
			0.26		0.23
0.29	*0.33*	*0.33*	*0.21*	*0.34*	*0.22*

Note: Given notation, "cell#(counter)", refers to scintillation cell (ranging from 1-6), analyzed on counter (1 or 2). For example, "1(1)" translates to cell #1, analyzed on counter #1.

averaging ~0.87 (87%) (Table 2.2). For sample calculations, a running average of cell efficiency was used according to cell number and counter.

Procedural blanks, which include both extraction board and acid blanks, consisted of ~300-400 mL of 1.5 N HCl. Differences in blank value (dpm g^{-1}) were apparent over time for the two extraction systems (Table 2.3). Blanks run on system B were relatively constant (~0.427 dpm g^{-1}), allowing a running average value to be used for sample correction. Fluctuations, however, were seen for blanks run on system A (0.539-1.007 dpm g^{-1}). To compensate for this artifact, a "date effective" blank value was calculated.

In addition to blanks, scintillation cell backgrounds were determined once every few weeks to correct for gradual accretion of residual ^{222}Rn onto the cells. Cell backgrounds averaged ~0.32 cpm, equating to ~75% of the blank value for extraction system B, and ~32-59% of the blanks for system A (Table 2.4). A running average for each cell, corresponding to cell number and counter, was used for sample correction.

2.4.3 Intercalibration of ^{222}Rn-Emanation and Gamma Spectrometry Methods

The ^{222}Rn-emanation and gamma spectrometry methods were intercalibrated using surface seawater samples having a range of ^{226}Ra activities. Comparison of ^{226}Ra activities (dpm g^{-1}) determined using the two different techniques indicate a high degree of correlation, with an R^2 = 0.93 over 36 samples (Figure 2.5). The intercalibration represents both MnA and MnB cartridge samples having activities ranging from

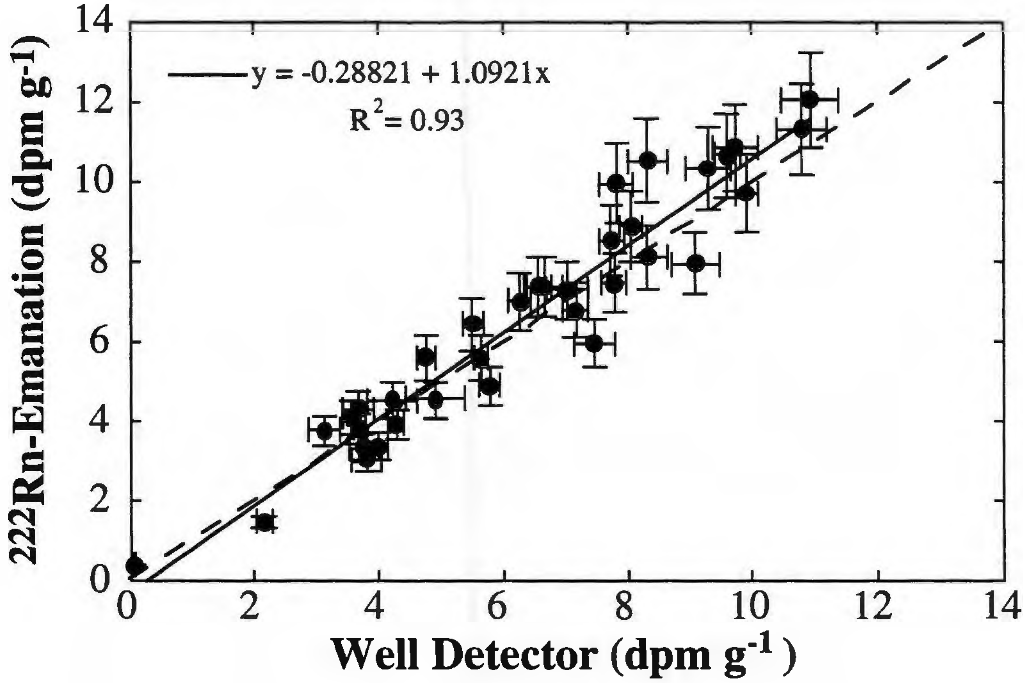

Figure 2.5 Intercalibration results of methods used to determine ^{226}Ra activities (^{222}Rn-emanation and gamma spectrometry).

approximately 0.5-12.0 dpm g^{-1}. Uncertainties for ^{222}Rn-emanation and gamma spectrometry average ± 0.66 and ± 0.24, respectively (Figure 2.5). The dashed line represents the 1:1 ratio for the two techniques.

2.5 Ancillary Methods

2.5.1 Salinity

Unfiltered salinity samples were collected in 500 mL acid-leached Nalgene bottles (triple-rinsed with the sample) and stored refrigerated. Salinity analysis was conducted at the National Marine Fisheries (NMFS) using a Guildline Autosal 8400A salinometer calibrated with standard IAPSO seawater.

2.5.2 Nutrients

Water samples were obtained to determine dissolved nutrients (nitrate, nitrite, ammonium and phosphate). Nutrient samples were initially collected in a triple-rinsed 500 mL Nalgene bottle, from which 50 mL was processed into acid-leached 125 mL Nalgene bottles using a Swin-lock filter-head apparatus with a Poretics GF-75 filter. Prior to filtering the nutrient sample, the syringe and 125 mL container were rinsed with approximately 20 mL of unfiltered and filtered sample, respectively. After collection, the samples were immediately frozen, either with dry ice or in a laboratory freezer. Analysis was completed at the University of Rhode Island using a Technicon Autoanalyzer (B. Buckley, analyst), following standard colorimetric methods (Lambert and Oviatt, 1986).

2.5.3 Organic Carbon

Particulate organic carbon (POC) and total organic carbon (TOC) samples were collected in acid-cleaned 500 mL Nalgene bottles and pre-combusted (575°C) 40 mL EPA standard amber vials, respectively. Prior to collection, all containers were triple-rinsed with sample water. TOC samples were frozen until analysis by high-temperature combustion at the State University of New York at Stony Brook (D. Hirschberg, analyst).

Particulate organic carbon samples were prepared by filtering through a Poretics 25 mm glass fiber filter (GF-75) with a 0.7 μm nominal pore size. Prior to filtration, all filters were wrapped in acetone-cleaned foil and combusted in a 575°C muffle furnace for twelve hours and stored in a sealed bag. Filtrate volumes ranged from 250-500 mL. POC sample filters were dried in a 50°C oven overnight. Wedges from each filter (equal to ~15-20% of the total area) were cut and weighed on a Mettler balance for mass fraction determination. The wedges were fumed with 12 N HCl for 12 hours in a dessicator and then dried overnight in a 50°C oven. The filter wedges were pelletized in tin caps and placed in well trays for storage. CHN analysis for determination of POC concentration was performed at the University of Rhode Island using a Carlo Erba Model 1106 Elemental Analyzer. POC concentrations were calculated from the standard curve and peak areas determined from CHN analysis (Pike and Moran, 1997).

Chapter 3

EVALUATING GROUND WATER INPUTS TO RHODE ISLAND'S SHELF WATERS AND SALT POND REGION

3.1 Introduction

The importance of ground water to coastal waters has become increasingly evident. Various studies have realized the significant role ground water plays as a transport mechanism, noting its carrying capacity of dissolved nutrients and materials to the coastal environment (Simmons, 1992; Valiela *et al.*, 1990; Lee and Olsen, 1985; Olsen and Lee, 1985). However, evaluation of ground water discharge has proven difficult in many near-shore budgets, due to its diffuse and time-varying nature.

In the southern region of Rhode Island, particularly the local salt ponds, ground water has traditionally been considered the primary source of fresh water (Lee and Olsen, 1985). However, studies concerning ground water in this region are limited. In particular, the suggested significance of ground water to the coastal lagoons of southern Rhode Island hinges on the validity of one study by the Coastal Resource Center (Grace and Kelly, 1981); in fact, this investigation represents the only known hydrological study of fresh water input to Rhode Island's salt ponds. This paucity of data raises the question as to whether ground water input to coastal waters of southern Rhode Island is well understood. The need for assessing ground water inputs to Rhode Island's coastal zone is essential, especially with respect to eutrophication issues affecting salt ponds and coastal management initiatives for nutrient control.

In the past, radium, a naturally-occurring radionuclide, has proven useful as a tool for examining ocean mixing and water mass motion. Recent studies have extended its utilization by demonstrating the potential of radium isotopes for evaluating ground water transport in the coastal environment. The sources of dissolved radium to coastal waters have been identified as open ocean water, river water, erosion of terrestrial sediments, desorption of river-borne particles and ground water, in addition to sediment-supported inputs for the case of salt marsh systems. Coastal enrichments of radium, specifically ^{226}Ra ($t_{1/2}$ = 1600 yrs), in shelf waters and salt marshes are reported to be the result of large ground water inputs (Moore, 1997, 1996; Rama and Moore, 1996). An implication of these recent studies is that consideration of these fresh water inputs to the coastal environment, with their carrying capacity of nutrients and materials, suggests the need for a re-evaluation of oceanic hydrological and geochemical mass balances.

The primary goal of this study is to investigate the use of ^{226}Ra as a tracer of ground water input to the coastal waters of southern Rhode Island. In this chapter, the first measurements of ^{226}Ra in this region are presented. From the distribution of ^{226}Ra within the salt ponds and adjacent shelf waters, an attempt will be made to quantify the magnitude of ground water inputs to these coastal waters.

3.2 Study Area

Southern Rhode Island's salt pond region encompasses an area of approximately 194 km^2, extending along the southern coast, bordering Block Island Sound and the southwest

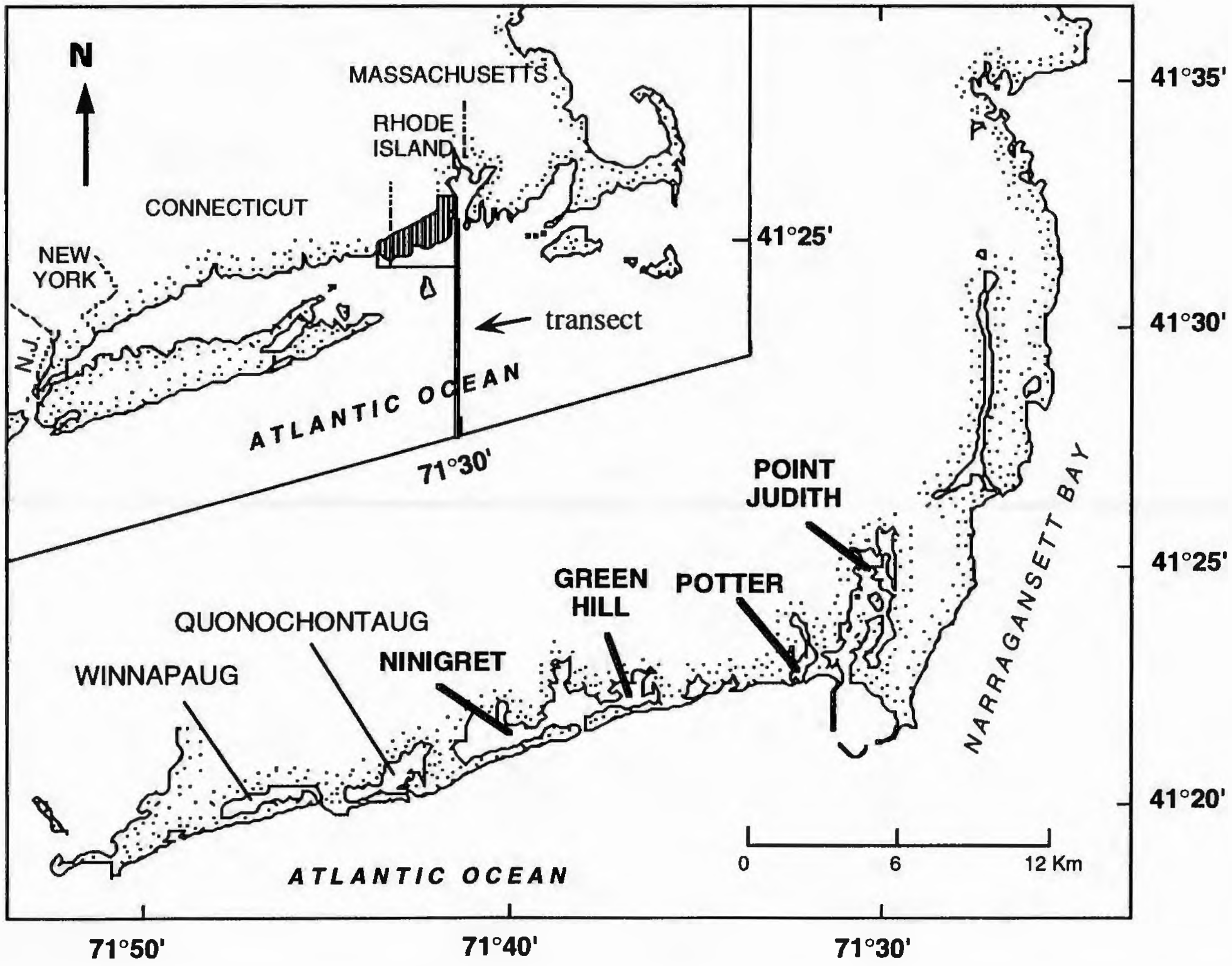

Figure 3.1 Map of Rhode Island study area, indicating the off-shore transect and coastal lagoon sampling locations (in **bold**).

Table 3.1 Southern Rhode Island salt pond characteristics (after Lee and Olsen, 1985 and Lee, 1980).

Pond	Area ($\times 10^6$ m^2)	Average Depth (m)	Tidal Range (cm)	Average Salinity (ppt)	Watershed Area ($\times 10^6$ m^2)
Point Judith	7.85	1.8	44.5	30	21.62[1]
Potter	1.35	1.8	20	27	9.91
Green Hill	1.55	0.8	3.7	23	16.13
Ninigret	6.45	1.2	13.7	28	28.48

[1] Excluding area of Saugatucket River watershed.

part of Narragansett Bay (Ely, 1990; Figure 3.1). The northeast reaches of the region are drained primarily by the Saugatucket and Pettaquamscutt Rivers, while the entire southern area is drained by a few permanent and intermittent streams flowing south into the salt ponds from the Charlestown Moraine ("Appraisal of the Ground Water Reservoir Areas in Rhode Island," 1961). In this study, the shelf waters adjacent to Rhode Island and those major ponds west of the Bay, Ninigret Pond, Green Hill Pond, Potter Pond and Point Judith Pond, will be investigated.

All four ponds are small and shallow, and characterized by brackish water (Boothroyd *et al.*, 1985; Lee and Olsen, 1985; Lee, 1980; Table 3.1). Permanent breachways built during the 1950's and 1960's have affected both the salinity and tidal flushing of the ponds. Over the last half-century, rapid residential growth throughout the salt pond region has affected the quality of Rhode Island's coastal watersheds, particularly due to nitrate input from lawn-care chemicals and sewage (Ely, 1990).

3.3 Methods and Sampling

3.3.1 Sampling

Coastal waters were sampled off southern Rhode Island during the summer of 1997 (June-August). An off-shore transect from Narragansett Bay to Block Island Canyon was performed by sampling surface waters at 12 stations aboard the *R/V Endeavor* during July 10-14, 1997 (Figure 3.2; Table 3.2). All surface samples were collected from the ship's

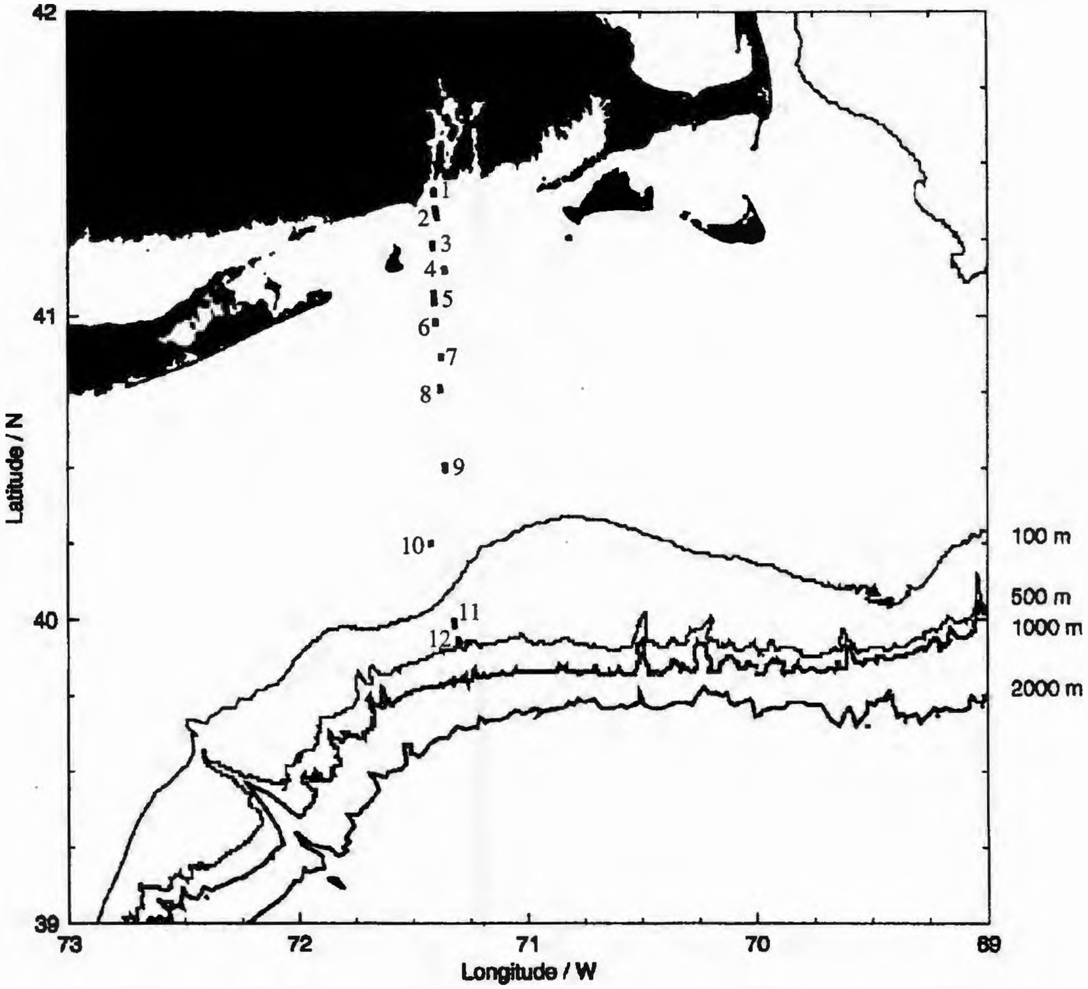

Figure 3.2 Location of stations sampled from Narragansett Bay to Block Island Canyon, during July 10-14, 1997.

Table 3.2 Location and distance along transect for sampling stations off southern Rhode Island, July 1997.

Station	Start of Sampling Lat(N),Long(W)	End of Sampling Lat(N),Long(W)	*Distance (km)
1	41° 23.49', 71° 24.24'	41° 25.15', 71° 24.55'	0.0
2	41° 23.49', 71° 23.46'	41° 21.50', 71° 23.98'	9.7
3	41° 14.68', 71° 24.77'	41° 12.78', 71° 24.69'	19.6
4	41° 08.39', 71° 21.55'	41° 09.65', 71° 21.81'	28.3
5	41° 05.00', 71° 24.61'	41° 02.09', 71° 24.36'	38.4
6	40° 59.42', 71° 24.04'	40° 58.20', 71° 23.90'	47.2
7	40° 51.36', 71° 22.43'	40° 52.55', 71° 22.36'	59.9
8	40° 46.50', 71° 23.00'	40° 44.98', 71° 22.89'	71.4
9	40° 30.91', 71° 21.68'	40° 29.06', 71° 21.48'	100.5
10	40° 14.58', 71° 25.32'	40° 15.70', 71° 25.27'	128.0
11	40° 00.17', 71° 19.18'	39° 58.38', 71° 19.03'	157.3
12	39° 48.49', 71° 17.14'	39° 48.70', 71° 17.41'	177.1

* Distance along transect (reference = Station 1).

salt water intake taps during transit to and from Station 12. Upon reaching each station, seawater samples were immediately collected for salinity, total organic carbon (TOC) and nutrient analyses. Water samples for ^{226}Ra analysis were collected in 55 gallon drums and pumped through two MnO_2 cartridges connected in-series (Figure 2.1). For each sample, 190-200 L of seawater was processed within approximately three hours.

In addition to the samples from the shelf waters, large-volume water samples were collected from 12 coastal lagoon sites and 9 residential ground water drinking wells in the southern Rhode Island region (Figure 3.3). All water samples were ~50-75 L and were pumped at a flow rate of 1-2 L min^{-1} through the MnO_2 cartridges. From each of the four salt ponds, sediment cores (~20-30 cm in length) were obtained for pore water and sediment-supported ^{226}Ra analyses. Ancillary samples were also collected for salinity, particulate organic carbon (POC) and nutrient data.

3.3.2 Analyses

Large-volume shelf water, salt pond and ground water well samples were analyzed for ^{226}Ra by gamma spectrometry using a well detector (Chapter 2). Small-volume, sediment pore water and sediment-supported ^{226}Ra activities were determined by ^{222}Rn-emanation (Mathieu *et al.*, 1988; Chapter 2). This method also served as a means of validating ^{226}Ra results obtained by gamma spectrometry. Ancillary analyses, including salinity, nitrate, nitrite, phosphate, ammonium ion, particulate organic carbon and total organic carbon, are described in Chapter 2.

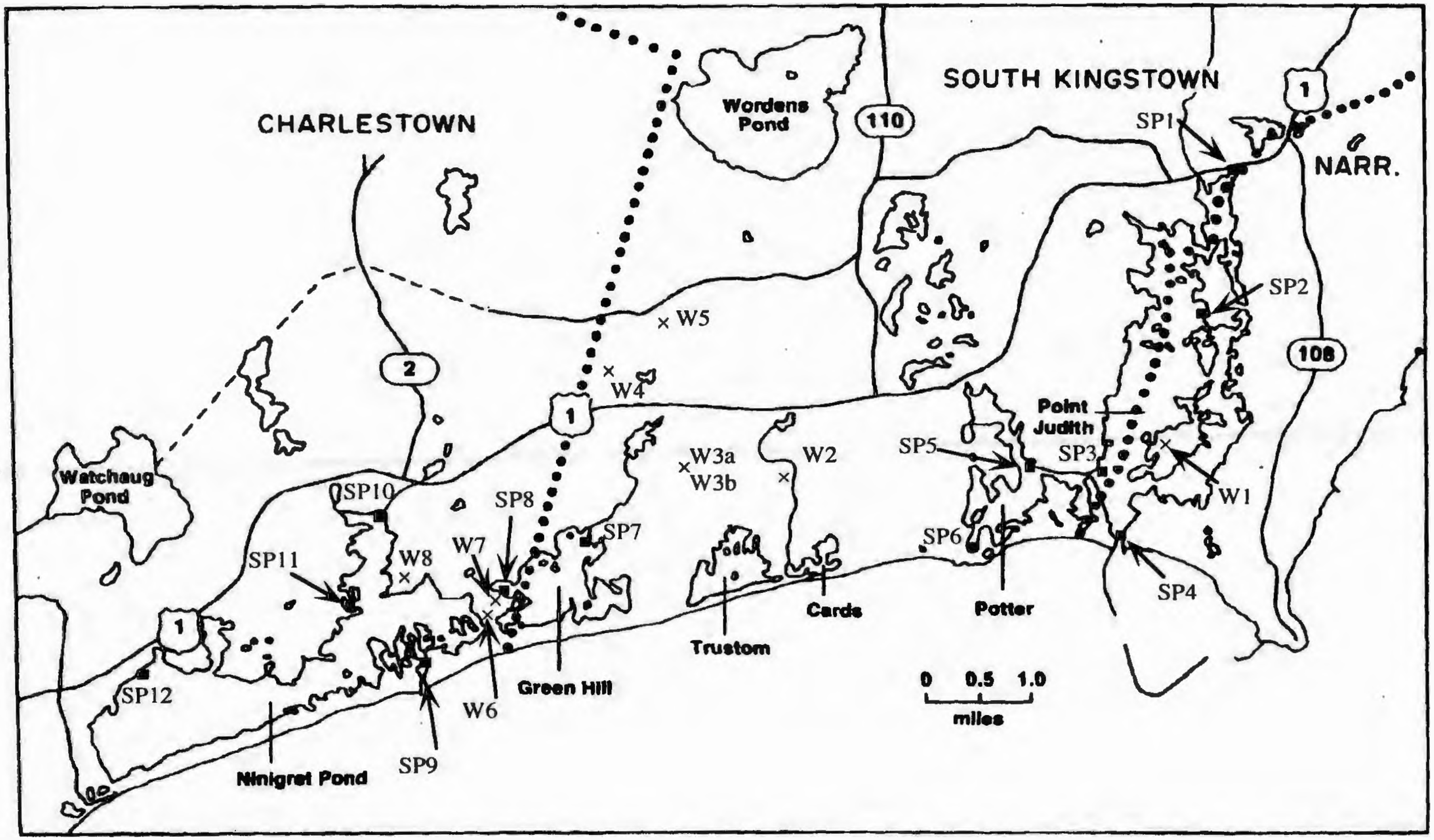

Figure 3.3 Map of residential ground water well (X) and salt pond locations (■) in southern Rhode Island sampled in this study.

3.4 Results and Discussion

3.4.1 Southern Rhode Island Shelf Waters

To determine ground water inputs to the coastal waters off southern Rhode Island, distributions of ^{226}Ra in residential ground water wells, shelf waters and possible river contributions were investigated. All results were collected during summer 1997.

3.4.1.a Off-shore Transect

Salinity and ^{226}Ra results for the transect performed off southern Rhode Island during July 1997 are shown in Figure 3.4. For the 12 stations sampled, ^{226}Ra activities range from 9.00-12.38 dpm 100 L^{-1}, with salinity values from 30.76-34.04 ppt (Table 3.3). No distinct radium gradient is observed along the transect, although the inner shelf waters (i.e. inner ~10 km from coast) tend to exhibit slightly higher ^{226}Ra activities on average. The lower ^{226}Ra activities encountered at Stations 3, 4 and 5 were initially thought to be the result of mixing with higher salinity, lower radium, open ocean water. Upon inspection of the salinity measurements for these stations, however, this hypothesis is not warranted, as the water is not significantly more saline. In fact, differences in ^{226}Ra activity along the transect cannot be entirely explained by changes in salinity, since salinity appears to be relatively constant for the entire sampling duration. The only exception would be that of Station 12 (~180 km from shore), where the drop in ^{226}Ra activity is characterized by more saline water.

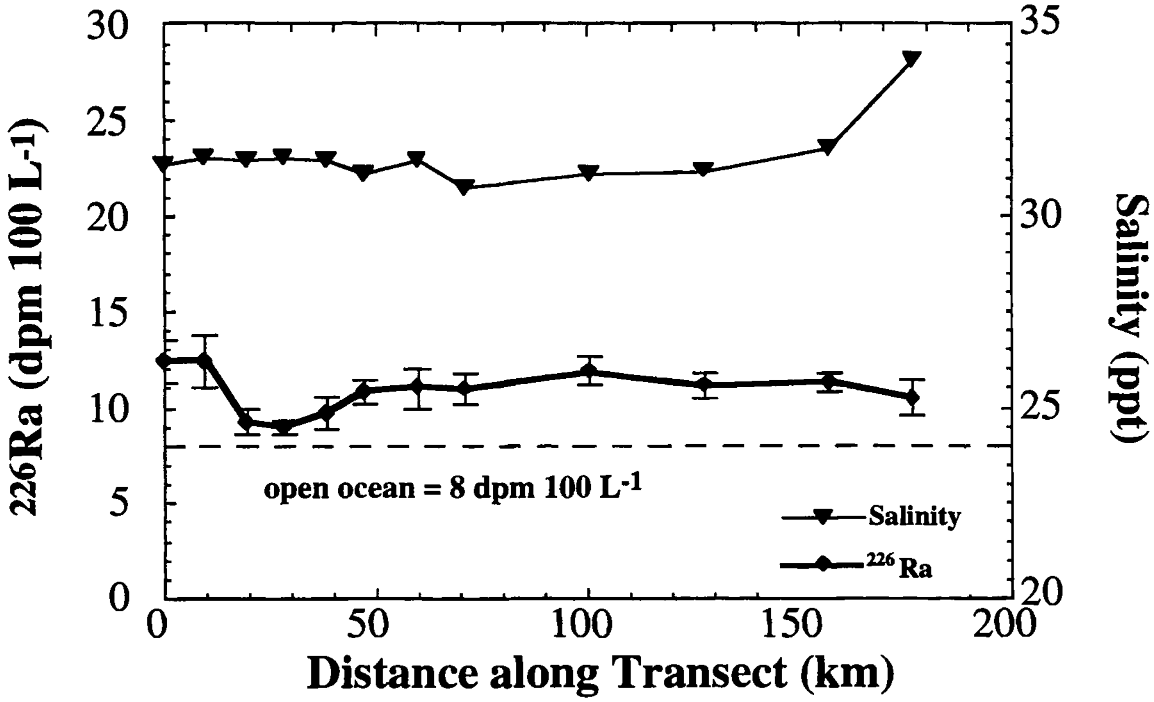

Figure 3.4 Salinity and ^{226}Ra activity along a transect across the shelf from Narragansett Bay to Block Island Canyon, sampled July 10-14, 1997.

Table 3.3 ^{226}Ra activities and ancillary data for stations sampled off-shore Rhode Island, July 1997.

Station	*Distance (km)	^{226}Ra Activity (dpm 100 L^{-1})	Salinity (ppt)	NH_4^+ (µM)	NO_3^- (µM)	NO_2^- (µM)	PO_4^{-3} (µM)
1	0.0	12.37 ± 1.93	31.377	0.86	0.39	0.03	0.55
2	9.7	12.38 ± 1.93	31.531	0.56	0.37	0.01	0.23
3	19.6	9.23 ± 1.42	31.491	2.04	0.62	0.01	0.20
4	28.3	9.00 ± 1.26	31.528	0.38	0.37	0.02	0.24
5	38.4	9.72 ± 1.35	31.501	1.56	0.47	0.03	0.30
6	47.2	10.81 ± 1.53	31.130	0.84	0.37	0.01	0.23
7	59.9	11.03 ± 1.71	31.465	0.24	0.33	0.08	0.08
8	71.4	10.95 ± 1.61	30.758	1.37	0.43	0.05	0.26
9	100.5	11.85 ± 1.60	31.136	1.40	0.58	0.01	0.22
10	128.0	11.12 ± 1.55	31.200	0.13	0.30	0.01	0.24
11	157.3	11.33 ± 1.08	31.773	0.20	0.38	0.01	0.24
12	177.1	10.48 ± 1.72	34.037	0.16	0.30	0.01	0.21

* Distance along transect (reference = Station 1).

The main objective in performing the transect was to evaluate ^{226}Ra distributions from shore, specifically in the shelf waters, and determine whether these activities were the result of ground water input to the region. While Moore's data (1996) for the SAB focused on determining ground water inputs to the inner shelf region due to large ^{226}Ra enrichments, this research did not encounter such elevated near-shore activities. However, for the entire length of the transect off southern Rhode Island, determined ^{226}Ra activities do show evidence of enrichment when compared to accepted open ocean values of 8.0 ± 0.5 dpm 100 L^{-1} (Moore, 1996). Specifically, ^{226}Ra activities in Rhode Island's coastal waters average 10.86 ± 1.11 (1σ) dpm 100 L^{-1} for the entire 180 km shelf (Table 3.3). Based on these measured activities, an excess of ^{226}Ra (average shelf activity minus open ocean activity) of ~3 dpm 100 L^{-1} is observed for the Rhode Island shelf waters. Further evaluation is required to determine to what extent these shelf enrichments are supported by ground water.

3.4.1.b Shelf Water Radium Box Model Assumptions

In order to evaluate the observed ^{226}Ra enrichments with regards to river contributions and ground water estimations, a box representing the volume of shelf water enriched in ^{226}Ra is assumed. For this research, the box dimensions are chosen according to the available transect data and based on assumptions concerning fresh water behavior. As enrichments are observed along the length of the transect in comparison to open ocean values, a distance of 180 km is chosen for the length of the box constrained by the transect data. Since only one transect was performed off southern Rhode Island, the width of the box is more difficult to constrain; to address the lack of data, however, a square box is simply used (180 km x 180 km), providing an upper limit for ground water determinations. Lastly, it is assumed that the depth of the box is approximately 10 m, modeled after the assumptions of Moore (1996). Unlike Moore's study for the SAB, no data could be found concerning the presence of a strong pycnocline at 10 m depth for the Rhode Island shelf waters during summer 1997. This depth is chosen, however, based on the assumption that fresh water discharged into Rhode Island's shelf region most likely comes from aquifer sources underlying the coastal waters. Therefore, discharged fresh water (i.e. ground water), if from localized, channeled flow, might rise through the overlying saltier water to the surface layers due to density differences. Overall, a box volume of ~3 x 10^{14} L is assumed for the region of ^{226}Ra enrichment off southern Rhode Island.

In addition, a flushing rate of ~30 days is assumed for the Rhode Island shelf box model. Although the actual residence time of these waters is not documented, this assumption is based on considerations of water movement in the region and published water residence times for neighboring water masses. Turekian *et al.* (1996) determined the residence time of Long Island Sound to be between 166 and 63 days based on ^{228}Ra-measured transfer rates. In comparison to the relatively protected waters of Long Island Sound, the shelf waters off southern Rhode Island are less sheltered and experience more exchange with neighboring waters, thus a shorter residence time. However, waters off southern Rhode Island are characterized by eddy circulation which may entrap water in the area, resulting in possible longer residence times (Kincaid, 1998). For the large area assumed in the box model calculations, an estimated residence time on the order of 30 days seems appropriate based on these assumptions.

3.4.1.c River Contributions

In order to quantify the contribution of ^{226}Ra from rivers to the shelf waters, an estimate of river discharge into the area is required. From published U.S. Geological Survey Water Resources data for the Massachusetts, Rhode Island and Connecticut region (Davies *et al.*, 1997; Socolow *et al.*, 1997), gauging stations for the North Atlantic Slope Basins immediately along the coast were selected to determine the flux of river water and suspended sediment to the shelf. Stations were chosen due to their location with regards of representing the total discharge from each drainage basin. For each station, average values were calculated for the June-August 1997 study period. In addition, discharge rates for smaller streams entering Rhode Island's shelf waters via local salt ponds were considered. As data is not available from USGS sources due to the small size of these streams, information was taken from a regional salt pond stream study (Ernst, 1996) for comparable water conditions (i.e. steam flow, ground water levels). In total, the average river discharge to Rhode Island's shelf waters for the 1997 summer period is estimated to be ~2.66×10^{10} L d^{-1} (Appendix B, Table B.1).

Average suspended particulate matter (SPM) concentrations are also listed in Appendix B (Table B.1). However, since suspended sediment data are not available for all of the rivers, estimates of SPM concentration are assumed considering the maximum estimates

Table 3.4 Estimated river contribution of ^{226}Ra ($^{226}Ra_{river}$) to the shelf waters of southern Rhode Island. Total riverine supply of ^{226}Ra includes both sediment (desorbed) and river (dissolved) inputs. Details concerning calculations are reported in Appendix B, Table B.2.

	$^{226}Ra_{river}$ (dpm 100 L^{-1})	*Percent of $^{226}Ra_{ex}$ Supported by Rivers
assumed SPM (mg L^{-1}):		
50	0.034	1.15%

* Based on an "excess" ^{226}Ra activity (i.e. shelf minus open ocean ^{226}Ra activity) of 3 dpm 100 L^{-1}.

of Moore (1996) for the SAB (~50 mg L^{-1}). Assuming that these sediment loadings for the rivers along the Southeastern U.S. are greater than those of New England due to differences in geology (silty material vs. mixed outwash and till), a SPM concentration of 50 mg L^{-1} might be considered an overestimate. For this reason, desorbable contributions calculated using this value may be many times greater than actual values for the rivers discharging into Rhode Island's shelf, thereby resulting in an overestimate of ^{226}Ra river input.

^{226}Ra river contribution ($^{226}Ra_{river}$), including both dissolved[3] and desorbable components, is calculated using Eq. 2.1 and listed in Table 3.4. Total riverine supported activity (i.e. 0.034 dpm 100 L^{-1}) is 2 orders of magnitude lower than the ^{226}Ra activities determined in the shelf waters. Using this estimate, rivers are capable of supplying ~1% of the observed Rhode Island shelf radium enrichments. Therefore, additional sources of ^{226}Ra are needed to support this excess ^{226}Ra.

Alternatively, an evaluation as to whether rivers discharging into the shelf are capable of supporting the measured coastal ^{226}Ra activities can be made by examining Figure 3.5. In this figure, ^{226}Ra activity is plotted against salinity for surface water samples from both

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[3] There are no measurements of dissolved ^{226}Ra activity for rivers in this study. Values are assumed to be comparable to those measured for a well-studied, neighboring river system, the Hudson River Estuary, in which activities on the order of ~4 dpm 100 L^{-1} have been determined (Li and Chan, 1979).

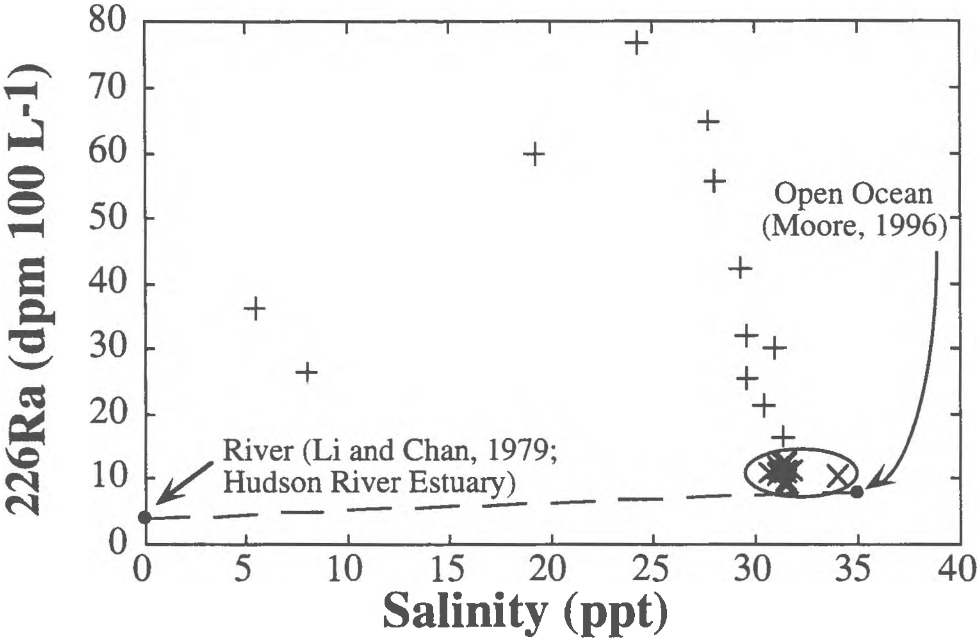

Figure 3.5 Plot of ^{226}Ra activity versus salinity for salt pond (+) and transect (× - enclosed in oval) samples in southern Rhode Island.

the salt ponds and coastal waters of southern Rhode Island. The dashed line represents the binary mixing curve between open ocean water (8 dpm 100 L^{-1}, 35 ppt; Moore, 1996) and dissolved river contributions (4 dpm 100 L^{-1}, 0 ppt; Li and Chan, 1979). From this plot, it is evident that for Rhode Island coastal waters which are characterized by an average of ~11 dpm 100 L^{-1}, 32 ppt, river water contributions cannot supply the required radium to the shelf. In fact, rivers discharging into the study region would actually dilute the observed ^{226}Ra signal in the coastal ocean and, in effect, would reverse that of the expected off-shore gradient. For this reason, other inputs are needed to account for the excess ^{226}Ra off southern Rhode Island.

3.4.1.d Ground Water Contributions

For ground water flux calculations, local measurements of ground water ^{226}Ra activity in southern Rhode Island are required. Activities range from 6.55-136.30 dpm 100 L^{-1} for sampled residential ground water wells, with a mean of ~60 dpm 100 L^{-1} (Table 3.5; Figure 3.6). These activities, although less than the ^{226}Ra values discovered by Moore (1996) for brackish water in the North Inlet (~700 dpm 100 L^{-1}), are high relative to riverine and open ocean values.

Variations in ^{226}Ra activity in the ground water wells appear to be a function of well depth and location (Figure 3.6). For example, shallow wells (3-9 m in depth) tend to exhibit higher levels of ^{226}Ra on average than deeper wells. This is somewhat unexpected considering that these wells contain water from glacial till and outwash less than 15 m in

Table 3.5 ^{226}Ra activities and ancillary data for ground water wells sampled in southern Rhode Island's salt pond region, June-August 1997. Well location and ^{226}Ra distributions are illustrated in Figure 3.6.

Well	^{226}Ra Activity (dpm 100 L^{-1})	Salinity (ppt)	NH_4^+ (µM)	NO_3^- (µM)	NO_2^- (µM)	PO_4^{-3} (µM)	Depth (m)
GW1	136.60 ± 10.23	0.00	1.03	945.77	0.13	1.11	6
GW2	19.52 ± 3.36	0.00	1.54	143.38	0.10	0.59	4-6
GW3a	18.43 ± 2.37	0.00	1.01	58.30	0.04	3.63	70
GW3b	48.29 ± 3.84	0.00	1.37	15.29	0.05	0.12	9
GW4	6.55 ± 1.06	0.00	2.05	11.27	0.07	0.25	23
GW5	56.33 ± 6.08	0.00	1.35	12.72	0.04	0.27	26
GW6	79.27 ± 9.37	0.00	1.01	187.34	0.03	0.13	--
GW7	68.07 ± 7.09	0.00	4.03	115.36	0.20	0.13	6-8
GW8	109.16 ± 7.39	0.00	0.30	92.03	0.03	0.04	3-4

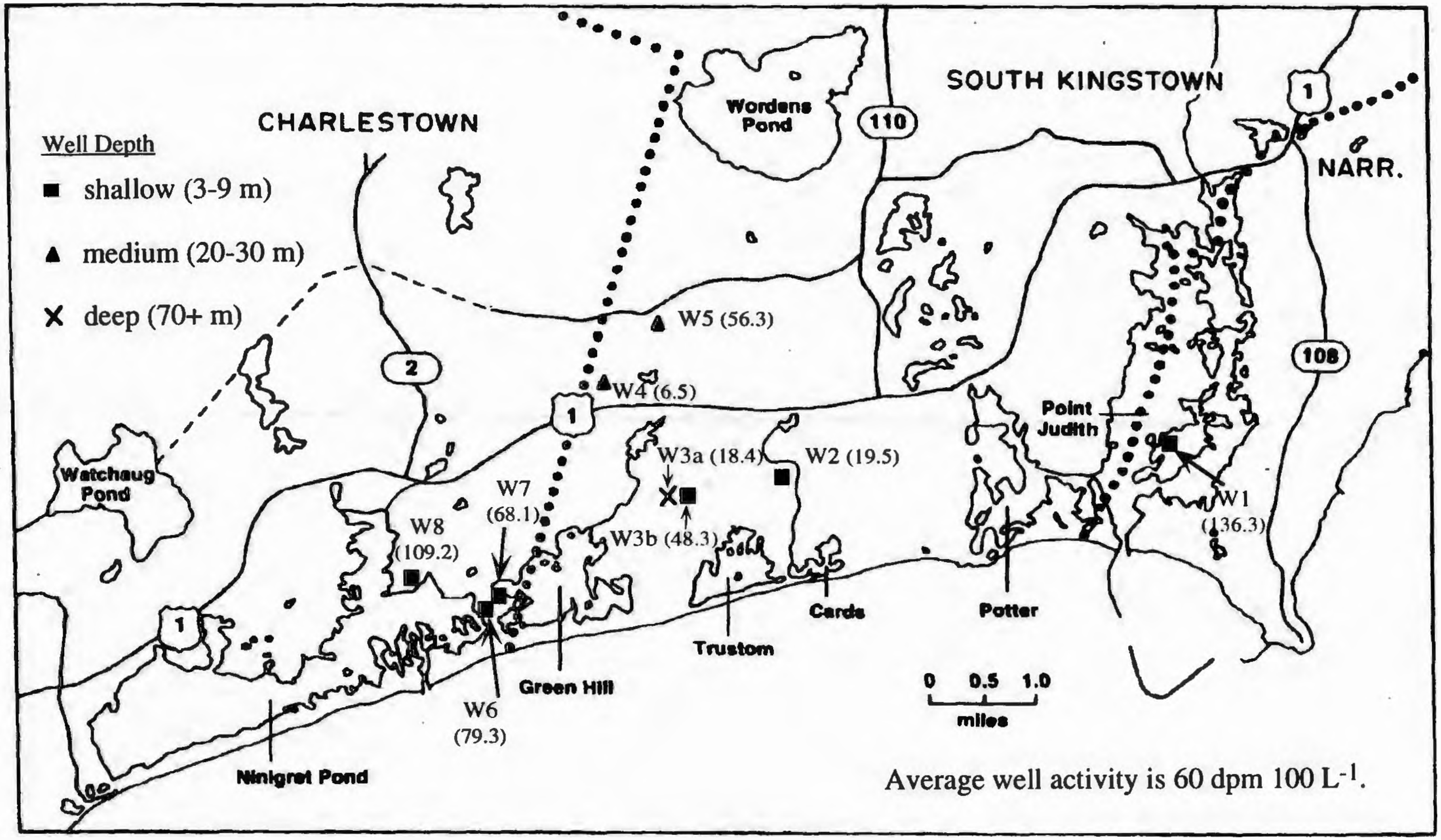

Figure 3.6 Map indicating distribution of residential ground water well locations in southern Rhode Island sampled in this study. Numbers in parentheses represent ^{226}Ra activities (dpm 100 L^{-1}) for the corresponding well.

depth ("Appraisal of the Ground Water Reservoir Areas in Rhode Island," 1961), instead of from deeper bedrock, assumed to be ^{226}Ra-rich. In addition, greater ^{226}Ra activities are more likely found in wells near sources of brackish water (i.e. the edges of salt ponds) or in salinized coastal aquifers. Salt water contamination of coastal ground water sources can occur due to changes in sea level, rupturing of aquifers from dredging practices and increased ground water use resulting in a landward movement of salty water into local aquifers (Moore, 1996). Within the salt pond region of southern Rhode Island, salt water intrusion has been normally recognized as a potential ground water problem (Trench, 1991; Hahn, 1959). Contrary to these previous ground water surveys for the south coastal region, however, the wells examined in this study do not exhibit any salt water contamination (Table 3.5), which could result in a higher ^{226}Ra activity (Moore, 1996).

Using the well ^{226}Ra activities, the flux of submarine ground water to Rhode Island's shelf waters is determined by means of a radium box model (Eq. 2.2; Section 3.4.1.b; Appendix B, Table B.3), listed in Table 3.6. Radium results indicate an excess of ^{226}Ra ($^{226}Ra_{ex}$) of 1.85 dpm 100 L^{-1}. To support this ^{226}Ra enrichment, ground water inputs ranging from ~2.0-10.0 x 10^{11} L d^{-1} for ground water well activities varying from 20-100 dpm 100 L^{-1} are needed. Compared to the total mean river discharge to Rhode Island's inner shelf, ground water fluxes are ~8-38 times greater (Table 3.6). Overall, these results suggest that submarine ground water represents an important source of fresh water to the coastal waters off southern Rhode Island.

Table 3.6 Submarine ground water input to Rhode Island's shelf waters during summer of 1997. Fluxes were calculated using ^{226}Ra ground water activities (20-100 dpm 100 L^{-1}) and shelf ^{226}Ra enrichments (^{226}Ra$_{ex}$), described in Appendix B, Table B.3.

^{226}Ra Ground Water Activity (dpm 100 L^{-1})	^{226}Ra$_{ex}$ for Shelf Waters (dpm 100 L^{-1})	Ground Water Flux (L d^{-1})	Ground Water / River Water
20 (minimum)	1.85	9.99 x 10^{11}	38
60 (average)	1.85	**3.11 x 10^{11}**	**13**
100 (maximum)	1.85	2.00 x 10^{11}	8

3.4.1.e Watershed Recharge Calculations

"Recharge" refers to an aquifer's ability to replenish local ground water reservoirs, due to water removal via natural and man-made processes. Crude watershed recharge calculations were conducted to determine whether the regional ground water reservoirs could support the estimated submarine ground water fluxes to the shelf (Appendix B, Table B.4).

For the coastal region of southern Rhode Island, first-order recharge estimates were determined based on assumptions of aquifer recharge rates (mean and maximum values; Grace and Kelley, 1981), as well as considering watershed area (Appendix B, Table B.4). Three different methods were used to evaluate the recharge capacity of southern Rhode Island's watersheds. The first method is based on a study by Grace and Kelley (1981), one of the few published reports pertaining to ground water inputs in southern Rhode Island. However, since the indicated drainage basin areas determined from water table elevations for this method are only for the regions immediately surrounding the salt ponds and are in some cases underestimates (i.e. Point Judith watershed area neglects the Saugatucket River basin), the recharge values calculated using this data are lower than expected. This method, however, provides useful estimates of recharge rates (1.3 ft yr^{-1} and 2.1 ft yr^{-1}) for mixed till and outwash in Rhode Island's coastal region.

For Methods 2 and 3, estimated recharge rates for mixed till and outwash from Grace and Kelley (1981) are again used, as no other values are available, with variations made in the

Table 3.7 Watershed recharge estimations for southern Rhode Island coastal area. Details of recharge calculations are given in Appendix B, Table B.4.

Calculation Method	Ground Water Recharge Estimates (L d^{-1}) (mean)	 (maximum)
1. Grace and Kelley, 1981	8.93×10^7	1.41×10^8
2. "Appraisal of the Ground Water Reservoir Areas in Rhode Island," 1961	2.12×10^8	3.41×10^8
3. U.S. Geological Survey web pages, (http://h20-nwisw.er.usgs.gov/nwis-w, 1998)	6.14×10^9	9.84×10^9

total watershed area under consideration. In the second calculation method, only the very southern reaches of Rhode Island extending over an area of 194 km^2 are considered, representing the ground water reservoir area for Rhode Island's south coastal area ("Appraisal of the Ground Water Reservoir Areas in Rhode Island," 1961). This area, though, is less than the actual watershed area for coastal Rhode Island (i.e. Pawcatuck-Wood basin), and therefore potentially underestimates ground water recharge. However, in Method 3, recent areal data from U.S. Geological Survey web pages (http://h20-nwisw.er.usgs.gov/nwis-w, 1998) are used for the river basins discharging into Narragansett Bay and the shelf waters off southern Rhode Island to determine ground water recharge. Eleven drainage basin areas are considered in the calculations, including the Taunton, Ten Mile, Blackstone, Moshassuck, Woonasquatucket, Pawtucket, Potowomut, Pawcatuck, Thames, Quashnet and Slocums river basins. Due to the timeliness and accuracy of this data, crude recharge estimates calculated using these more realistic drainage basin areas are most likely representative of actual values.

For the three different calculation methods, ground water recharge estimates range from ~1-98 x 10^8 L d^{-1}, listed in Table 3.7. Considering the previous discussion of each of the methods, however, estimated ground water recharge values are most likely on the order of ~10^9 L d^{-1} (Method 3). Note, however, that these values are likely an upper limit of recharge potential for the study region during the summer 1997 period, as the recharge rates used in the calculations are for yearly conditions and specifically for the glacial mixed till and outwash deposits of southern Rhode Island. Applying these rates to the larger drainage basins in the southern New England characterized by less permeable geology may be an overestimate. Overall, the recharge estimates are approximately an order of magnitude less than the calculated submarine ground water inputs of 3.33×10^{11} L d^{-1} (± 73.95%) for Rhode Island's shelf waters (Table 3.6). These results indicate that the ground water reservoirs of southern Rhode Island are most likely not potentially capable of supporting the ^{226}Ra-based estimates of ground water input to the shelf waters.

3.4.1.e Ground Water Input to the Shelf Waters: Interpretation and Implications

The ^{226}Ra-based estimates of ground water flux determined in this research appear unrealistic in magnitude, suggesting an enormous flow of fresh water from ground water sources to the Rhode Island's shelf waters. The unreasonable suggestion of these flows is further emphasized when estimated ground water inputs are compared to total mean river discharge from all major rivers flowing into the region, indicating that the calculated ground water fluxes are on average ~13 times that of river input. Withstanding magnitude, these determined ground water flows could not adequately be supplied from local ground water reservoirs based on the crude watershed recharge calculations performed in this study, which are themselves considered overestimates.

Interesting to note, the ground water inputs calculated in this study are comparable to that determined by Moore (1996) of 7×10^{10} L d^{-1} for the coastal waters of the SAB, pertaining only to the inner shelf. If one were to use a box model for the coastal waters of Rhode Island similar in scope to Moore's approach for the SAB, specifically a box whose dimensions solely address the inner shelf (~4×10^{12} L, $\tau \sim 10$ days), enormous ground water flows would still be calculated (i.e. on the order of 10^{10} L d^{-1}) based on this radium approach. Compared to river input to the re-scaled study region or box (~10^{9} L d^{-1}), these ground water fluxes are again much greater (~8x). These calculations suggest that the size of the radium box used for determining ground water input to the shelf is immaterial, and that regardless of the dimensions used, the estimated ground water flows to Rhode Island's shelf waters will be unreasonably large.

From these anomalies, several implications arise concerning the estimations of ground water flux to Rhode Island's shelf waters determined in this study. The average ground water ^{226}Ra activity of ~60 dpm 100 L^{-1} for wells sampled in southern Rhode Island's salt pond region may not account for all possible ground water sources of radium in the region. As mentioned, these activities were determined for mostly shallow wells over a limited sampling area, characterized by slightly elevated ^{226}Ra activities. None of the ground water wells sampled, however, were comparable to the brackish ground water activity used in Moore's ground water calculations for the SAB (Moore, 1996). If indeed the ^{226}Ra ground water activity for southern Rhode Island is similar to that used by Moore (1996) of ~700 dpm 100 L^{-1}, the estimated ground water input to the Rhode Island shelf region based on any size box model would be one order of magnitude less, and would then be comparable to river discharge to the study area.

Possible explanations for the "missing radium" theory are that perhaps due to the limited scope of this study, deep wells characterized by high ^{226}Ra activity, presumably from bedrock sources, were not represented in the sampling. Another explanation could be that wells experiencing salt water contamination which would have resulted in higher ^{226}Ra activities were simply overlooked, or the occurrence of aquifer salinization in southern Rhode Island is affected by seasonal signals which could not be taken into consideration. Nevertheless, these findings suggest that additional sources of ^{226}Ra, unaccounted for in the ground water sampling of this study, may exist in the salt pond region of southern Rhode Island.

Overall, the ^{226}Ra-based ground water estimations determined in this study to Rhode Island's shelf waters pose questions that are difficult to answer in the scope of this research, pointing to a further evaluation of ^{226}Ra as a ground water tracer to the near-shore waters of southern Rhode Island.

3.4.2 Rhode Island's Salt Pond Region

To evaluate submarine ground water input to Point Judith, Potter, Green Hill and Ninigret ponds, ^{226}Ra distributions were determined for each individual coastal lagoon, including pore water and sediment-supported activities, in addition to contributions from streams and rivers flowing into the ponds. As with ground water calculations for Rhode Island's shelf waters, all salt pond data pertains to the June-August 1997 study period.

3.4.2.a Coastal Lagoons

Surface water results for the 12 sampled coastal pond locations are listed in Table 3.8, with the distribution of ^{226}Ra activity throughout the salt pond region illustrated in Figure 3.7. ^{226}Ra activities range from ~17-77 dpm 100 L^{-1} for surface salt pond waters collected over a range of tidal conditions and salinity (5.4-31.3 ppt) (Table 3.8). Average ^{226}Ra activities for each of these coastal lagoons range from ~32-57 dpm 100 L^{-1}.

^{226}Ra results for Rhode Island's salt ponds are comparable in magnitude to those measured by Rama and Moore (1996) during the summer of 1993 for the North Inlet salt marsh. However, unlike the study performed by Rama and Moore, variability in ^{226}Ra activity for most of the salt ponds of southern Rhode Island can not be easily explained by considering the time of sampling (i.e. tidal stage). For instance, salt pond locations exhibiting higher activities of ^{226}Ra are not necessarily associated with low or ebbing tides drawing Ra-enriched, low salinity ground water from local aquifers (Table 3.8), as

Table 3.8 ^{226}Ra activities and ancillary data for salt pond locations sampled throughout southern Rhode Island's salt pond region, June-August 1997. Refer to Figure 3.7 for distribution of ^{226}Ra activities and exact sample location. (Note: Errors represent 1σ).

Salt Pond	Tide Stage	^{226}Ra Activity (dpm 100 L^{-1})	Salinity (ppt)	POC (μM)	NH_4^+ (μM)	NO_3^- (μM)	NO_2^- (μM)	PO_4^{-3} (μM)
Point Judith:	$^{226}Ra_{avg}$ = 33.50 ± 18.75 dpm 100 L^{-1}; $^{226}Ra_{PW}$ = 0.005 ± 0.001 dpm mL^{-1}; sediment-supported ^{226}Ra = 0.64 dpm g^{-1}							
SP1	mid (flood)	59.94 ± 10.66	19.189	51.17	10.18	18.03	0.66	0.44
SP2	mid (flood)	32.02 ± 5.77	29.587	89.55	1.99	1.04	0.11	0.67
SP3	low-mid (flood)	25.58 ± 4.75	29.631	37.66	2.78	3.03	0.08	0.54
SP4	mid (flood)	16.46 ± 2.17	31.365	18.16	2.16	0.96	0.13	0.66
Potter:	$^{226}Ra_{avg}$ = 31.78 ± 14.98 dpm 100 L^{-1}; $^{226}Ra_{PW}$ = 0.005 ± 0.0007 dpm mL^{-1}; sediment-supported ^{226}Ra = 0.24 dpm g^{-1}							
SP5	low	21.19 ± 3.44	30.412	80.24	1.72	0.54	0.05	0.41
SP6	high-mid (ebb)	42.38 ± 3.98	29.268	33.86	7.41	0.68	0.20	0.47
Green Hill:	$^{226}Ra_{avg}$ = 56.59 ± 28.78 dpm 100 L^{-1}; $^{226}Ra_{PW}$ = 0.009 ± 0.0007 dpm mL^{-1}; sediment-supported ^{226}Ra = 0.32 dpm g^{-1}							
SP7	mid-low (ebb)	36.25 ± 4.33	5.400	49.45	3.55	7.27	0.14	0.25
SP8	mid-high (flood)	76.94 ± 10.29	24.293	--	13.56	4.73	0.26	0.22
Ninigret:	$^{226}Ra_{avg}$ = 44.18 ± 19.00 dpm 100 L^{-1}; $^{226}Ra_{PW}$ = 0.009 ± 0.004 dpm mL^{-1}; sediment-supported ^{226}Ra = 0.68 dpm g^{-1}							
SP9	mid-low (ebb)	29.98 ± 4.29	30.939	18.49	1.39	0.44	0.04	0.43
SP10	low	26.32 ± 4.48	7.929	33.48	4.08	6.39	0.18	0.48
SP11	high	55.62 ± 8.17	28.072	69.92	2.03	0.28	0.05	0.12
SP12	low-mid (flood)	64.90 ± 9.74	27.733	47.58	4.41	1.78	0.08	0.36

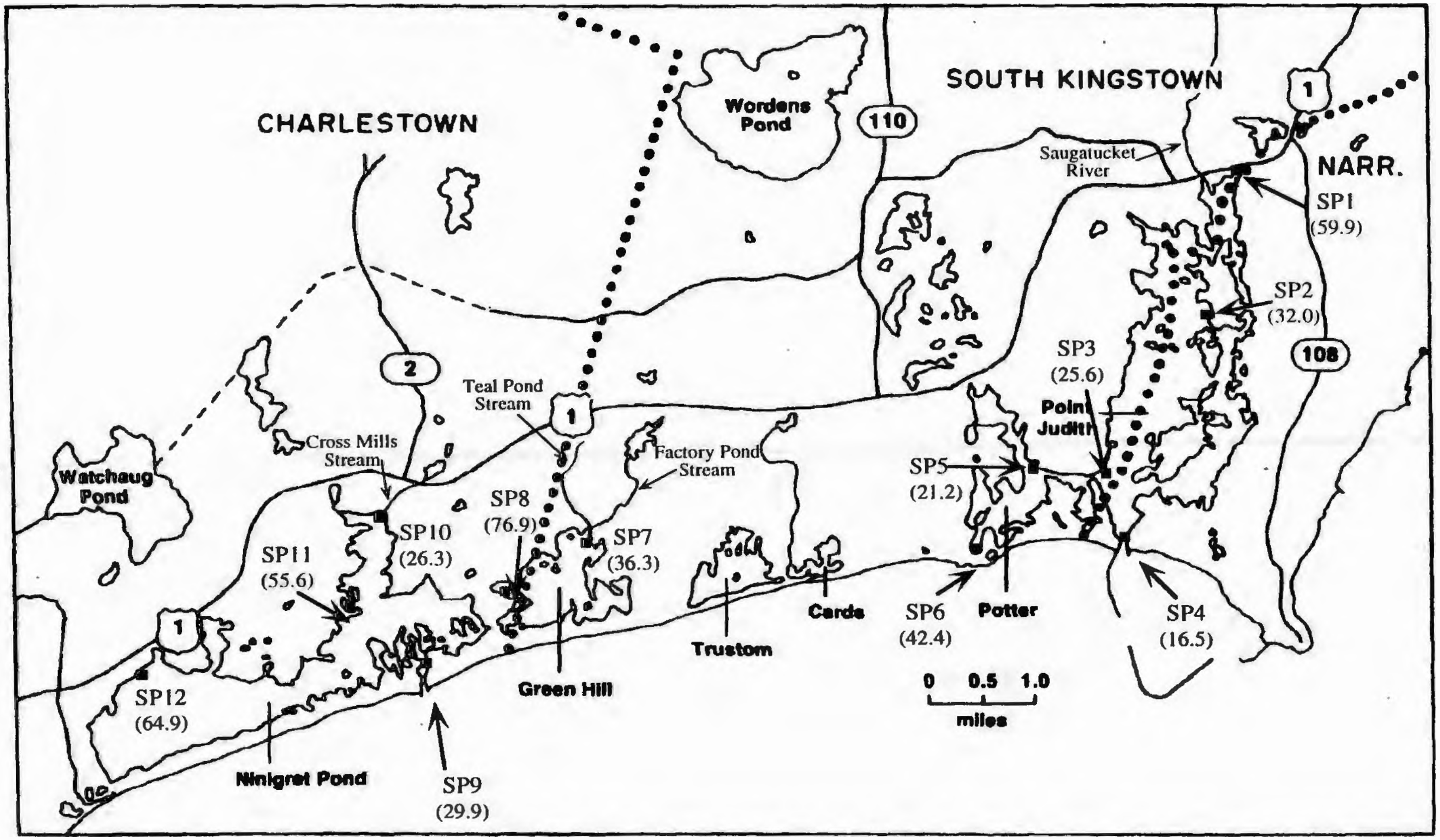

Figure 3.7 Map indicating distribution of ^{226}Ra activity within salt pond region of southern Rhode Island. Numbers in parentheses represent ^{226}Ra activities (dpm 100 L^{-1}) for the corresponding salt pond location.

hypothesized for the North Inlet marsh (Rama and Moore, 1996). Instead, other conditions such as the presence of fresh water from underground springs (or ground water) and proximity to permanent breachways (SP4, SP9) may explain variations in ^{226}Ra activity (Figure 3.7).

Supporting the suggestion that ^{226}Ra activity is related to salinity, however, is the distribution found within Point Judith Pond. Upon inspection, a distinct north to south gradient is seen in the sampled surface waters, with ^{226}Ra and salinity values ranging from ~60 dpm 100 L^{-1}, 31.4 ppt in the northern reaches of the pond to ~17 dpm 100 L^{-1}, 19.2 ppt in the southern region (Table 3.8; Figure 3.8). The distinction between the upper and lower areas of the pond can be explained by examining the water masses which contribute to each of the regions separately. In the northern reaches of Point Judith Pond, lower salinity values may reflect fresh water inputs entering the upper region of the pond (i.e. Saugatucket River inputs). However, as will be discussed in Section 3.4.2.c, river and stream water inputs to the salt pond region are on the order of ~1 dpm 100 L^{-1} and cannot therefore explain the higher ^{226}Ra activities. Other sources of fresh water, possibly large inputs of ground water seeping through the sediments to this area of the pond, may help to account for the elevated activities. As one heads south towards the lower region of the pond, the values of ^{226}Ra and salinity appear to be gradually influenced by the more saline, lower ^{226}Ra coastal water entering the breachway (SP4) (Table 3.8; Figure 3.8).

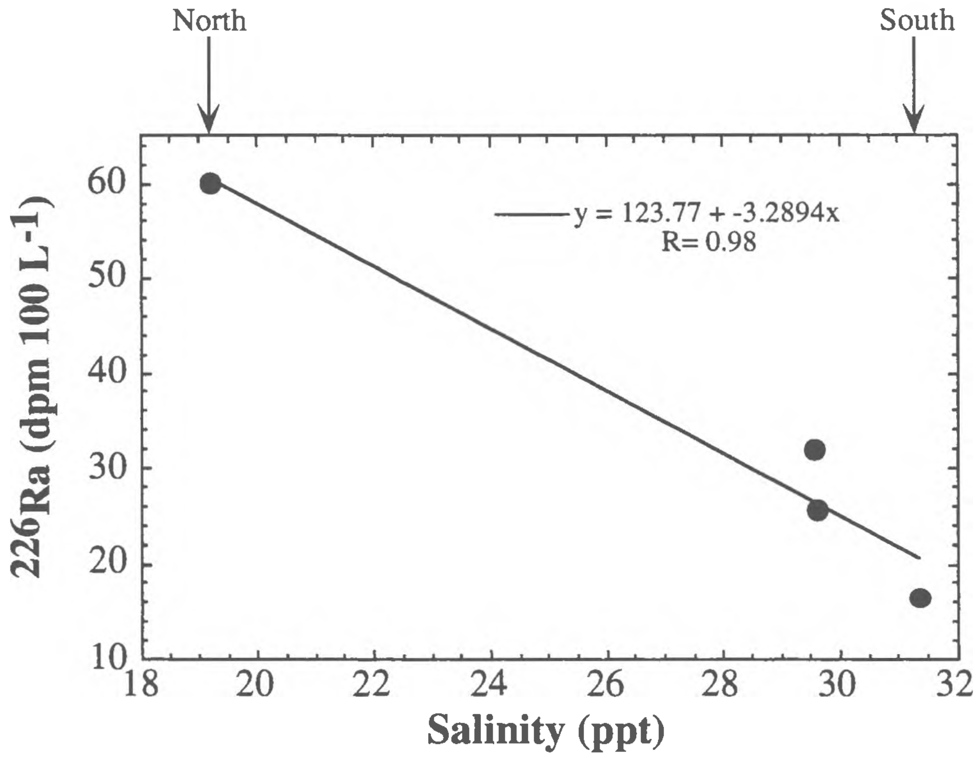

Figure 3.8 Correlation of salinity and ^{226}Ra activity for Point Judith Pond.

3.4.2.b River, Salt Pond Sediment and Pore Water Contributions

In addition to surface water activities, pore water activities ($^{226}Ra_{PW}$) and sediment-supported ^{226}Ra contributions from the upper ~5 cm of sediment were also evaluated from cores collected from each of the ponds (Table 3.8, 3.9). Pore water ^{226}Ra activities range from 0.005-0.009 dpm mL^{-1}, which are significant in magnitude (500-900 dpm 100 L^{-1}) and representative of the ground water component entering the salt ponds. The pore water influx of ^{226}Ra due to diffusion from below is ignored, as only the top 5 cm of the core yielded any pore water upon centrifuging due to the sandy nature of the salt pond sediments.

Sediment-supported ^{226}Ra activities range from 0.24-0.68 dpm g^{-1}, which are an order of magnitude less than the expected range of ^{226}Ra water sample activities for this study (~4-12 dpm g^{-1}; Figure 2.5). Due to their insignificance compared to water sample activities, the contribution of ^{226}Ra from the top layer of sediment can therefore be neglected for each of the ponds. In addition, influx of desorbable ^{226}Ra from surface sediments and sediments below the top 5 cm can be ignored due to the time-scales required for ^{226}Ra production from its parent, ^{230}Th (i.e. 500 years for 20% regeneration; Moore, 1996).

With regards to riverine contributions to Rhode Island's salt pond region, only the ponds of Point Judith, Green Hill and Ninigret receive fresh water from rivers (Figure 3.7). As mentioned in Section 4.4.1.b, U.S. Geological Survey discharge rates and suspended sediment data for these smaller streams are not available. For this reason, estimates for

Table 3.9 ^{226}Ra box model results and ground water influx to the salt ponds of southern Rhode Island. Details given in Appendix C, Table C.1.

Pond	^{226}Ra$_{ex,F}$ (dpm cm^{-2} d^{-1})	^{226}Ra Stream (dpm cm^{-2} d^{-1})	†Sediment-Supported ^{226}Ra (dpm g^{-1})	‡Pore Water Diffusion Influx (dpm cm^{-2} d^{-1})	^{226}Ra$_{influx}$ (dpm cm^{-2} d^{-1})	Ground Water Influx (dpm cm^{-2} d^{-1})	Pore Water ^{226}Ra (dpm mL^{-1})	Ground Water Influx (mL cm^{-2} d^{-1})
Point Judith	$3.29\text{x}10^{-4}$	$6.37\text{x}10^{-5}$	0.64	nil	$6.37\text{x}10^{-5}$	$2.65\text{x}10^{-4}$	0.005	0.053
Potter	$1.36\text{x}10^{-4}$	0.0	0.24	nil	0.0	$1.36\text{x}10^{-4}$	0.005	0.027
Green Hill	$5.58\text{x}10^{-5}$	$8.52\text{x}10^{-6}$	0.32	nil	$8.52\text{x}10^{-6}$	$4.73\text{x}10^{-5}$	0.009	0.005
Ninigret	$1.50\text{x}10^{-4}$	$7.13\text{x}10^{-6}$	0.68	nil	$7.13\text{x}10^{-6}$	$1.43\text{x}10^{-4}$	0.008	0.018

† Determined for top ~5 cm of sediment (sediment-supported ^{226}Ra activities are neglected, as are desorbable contributions – see Section 3.4.2.a).

‡ Assumed to be negligible due to sandy nature of sediments.

the Saugatucket River, Factory Pond, Teal Pond and Cross Mill Streams are made from past regional stream studies (Ernst, 1996; Appendix B, Table B.1) and based upon comparison to hydrological data for known locations in Massachusetts and Rhode Island (Socolow *et al.*, 1997). Maximum inputs from these rivers and streams to southern Rhode Island's salt ponds, including both dissolved and desorbable ^{226}Ra fractions, are estimated to be 0.18-1.06 dpm 100 L^{-1} (Table 3.9; Appendix C, Table C.1). When compared to the average ^{226}Ra pond activities (see Table 3.8), these contributions are a small fraction of the overall ^{226}Ra activity of each salt pond.

3.4.2.c ^{226}Ra Box Model Results and Estimated Ground Water Inputs

From the determined ^{226}Ra activities, possible submarine ground water inputs to each of the individual salt ponds for the summer 1997 study period are evaluated by means of a simple radium box model (Eq. 2.3, 2.4; Appendix C, Table C.1). ^{226}Ra inventories (export and input) and inferred ground water flux results for the four coastal ponds are listed in Table 3.9.

Export fluxes of ^{226}Ra from each salt pond, denoted as $^{226}\mathrm{Ra}_{ex,F}$ (Eq. 2.3), range from 5.58-32.9 x 10^{-5} dpm cm^{-2} d^{-1} (Table 3.9). Each ^{226}Ra flux value was determined by evaluating the excess or enrichment of ^{226}Ra ($^{226}\mathrm{Ra}_{ex}$) for each salt pond, which in turn is defined as the average salt pond activity corrected for contributions from near-shore waters off southern Rhode Island (i.e. ~11 dpm 100 L^{-1}; see Section 4.4.1.a). Neglecting possible ground water inputs, the export flux of ^{226}Ra from each pond should be balanced by the total influx from stream sources (dissolved and desorbed), pore water and sediment-supported ^{226}Ra activities. The total influx of ^{226}Ra ($^{226}\text{Ra}_{influx}$) to each of the four salt ponds is listed in Table 3.9, with values ranging from 8.52-63.7 x 10^{-6} dpm cm^{-2} d^{-1}. Comparison of $^{226}\text{Ra}_{ex,F}$ and $^{226}\text{Ra}_{influx}$ values in Table 3.9 indicates that additional inputs of ^{226}Ra to the salt ponds are required to balance the export fluxes. Through back-calculation, the source of necessary ^{226}Ra is determined to be from inputs of ground water to each of the ponds. Specifically, ground water fluxes ranging from 4.73-26.5 x 10^{-5} dpm cm^{-2} d^{-1} to these ponds are estimated for the study period.

In terms of hydrological flux units, these ground water values are converted using the determined $^{226}\text{Ra}_{PW}$ activities, which are representative of ground water seeping upwards through the bottom salt pond sediments (Appendix C, Table C.1). From these calculations, estimated submarine ground water inflows of 0.005, 0.018, 0.027 and 0.053 mL cm^{-2} d^{-1} are evaluated to the salt ponds of Green Hill, Ninigret, Potter and Point Judith, respectively (Table 3.9). Figure 3.9 illustrates a graphical comparison of the estimated ground water fluxes to each of the four ponds. The error bars represent those ground water values calculated based on a salt pond residence time of 30 days (± 50%), while the solid and dashed lines represent fluxes determined for the corresponding pore water activities (0.005, 0.008, 0.009 dpm mL^{-1}), over a range of $^{226}\text{Ra}_{ex}$ (10-60 dpm 100 L^{-1}) and tidal height (0-50 cm), bracketing the actual values.

Based on the area of each salt pond (Table 3.1) and the determined submarine ground water inputs (Table 3.9), ground water fluxes in units of L d^{-1} were calculated. The

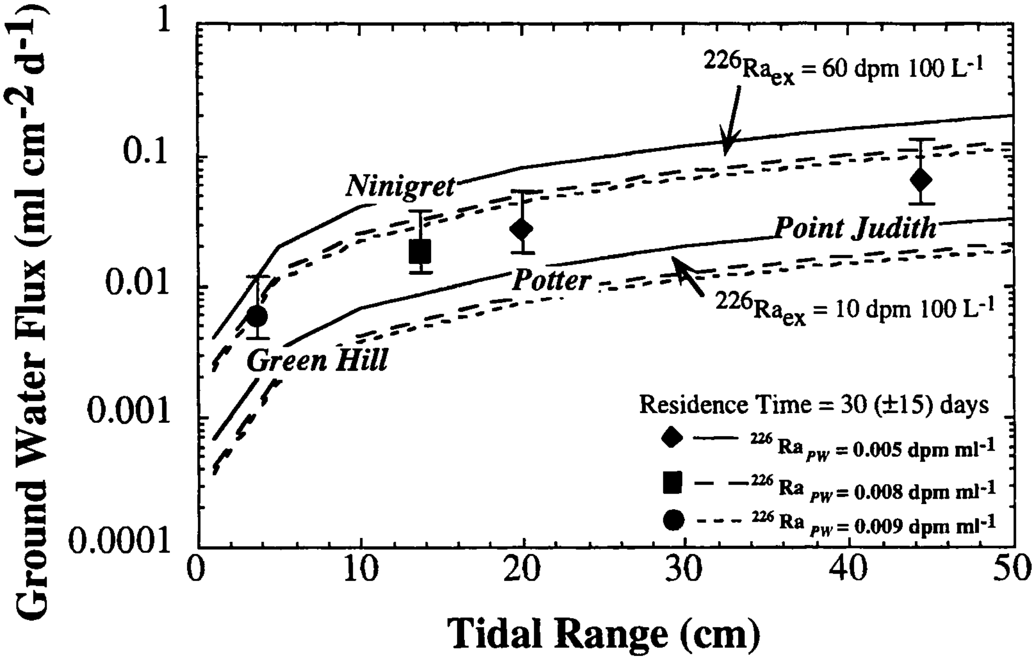

Figure 3.9 Comparison of ^{226}Ra-based estimates of ground water fluxes to salt ponds of southern Rhode Island.

Table 3.10 Comparison of ground water fluxes and river/stream inputs to Rhode Island's salt ponds for summer 1997.

Salt Pond	Ground Water Flux (10^5 x L d^{-1})	River/Stream Input (10^5 x L d^{-1})	$\frac{\text{River/Stream}}{\text{Ground Water}}$
Point Judith	41.6	1000	24
Potter	3.68	0	--
Green Hill	0.815	30	37
Ninigret	11.5	100	9

estimated values, listed in Table 3.10, range from ~1-42 x 10^5 L d^{-1} for the summer 1997 study period. These ground water inputs are in most cases an order of magnitude less than inputs of river or stream water into the ponds. These ^{226}Ra-based estimates suggest that ground water, as it pertains to the study period, may be less of an important transport mechanism to the coastal lagoons than previously considered (Ernst, 1996; Lee and Olsen, 1985).

Ground water results from this investigation are compared to those reported by Grace and Kelley (1981) for the Rhode Island salt pond region in Table 3.11. In most cases, the input of ground water to the salt ponds based on these two studies are offset by an order of magnitude. As summer periods are usually characterized by annual lows in stream discharge and ground water flow (Socolow *et al.*, 1997), the lower ground water values determined in this investigation for the summer of 1997 may indeed be typical considering the time frame of study. For example, USGS Water Resources Data for Massachusetts and Rhode Island (Socolow *et al.*, 1997) indicate that although ground water conditions during the summer months were in the normal range, water table levels were slightly low (~1-2 ft) compared to the rest of the year and would therefore result in lower ground water discharge.

Table 3.11 also indicates similar ground water trends between ponds for the two investigations, with the smaller coastal ponds of Potter and Green Hill receiving the least input of submarine ground water. For the larger ponds, note that in determining the ground water input to Point Judith Pond, the report by Grace and Kelley (1981) neglects

Table 3.11 Comparison of ground water fluxes determined in this study and by Grace and Kelley (1981). Ground water fluxes from this study pertain to summer 1997 values extrapolated to annual inputs. Ground water values for Grace and Kelley are calculated from a fresh water balance to each pond. Units are L yr^{-1} to each pond area.

Study	Point Judith	Potter	Green Hill	Ninigret
Grace and Kelley (1981):				
fresh water inflow	$2.53x10^{10}$	$5.00x10^{9}$	$6.80x10^{9}$	$1.50x10^{10}$
precipitation	$2.92x10^{9}$	$5.95x10^{8}$	$7.77x10^{8}$	$2.89x10^{9}$
runoff	$1.85x10^{9}$	0	0	0
stream	$9.50x10^{9}$	0	$3.32x10^{9}$	$2.57x10^{9}$
*Ground Water Input	*$1.10x10^{10}$*	*$4.41x10^{9}$*	*$2.70x10^{9}$*	*$9.54x10^{9}$*
This Study:				
Ground Water Input	*$1.52x10^{9}$*	*$1.34x10^{8}$*	*$2.97x10^{7}$*	*$4.20x10^{8}$*

* ground water = fresh water inflow - precipitation - runoff - stream

the Saugatucket River basin in their watershed area, while the ground water calculations in this study inherently include all the regional aquifers surrounding each individual salt pond. Since the method employed by Grace and Kelley calculates ground water flux by multiplying the watershed area surrounding each salt pond by an aquifer recharge rate (see Appendix B, Table B.4), the resulting ground water value for Point Judith Pond may perhaps be an underestimation. Considering this argument, if the Point Judith watershed area determined by Grace and Kelley were larger, the two studies would exhibit a more similar trend regarding ground water flux for the larger ponds of Point Judith and Ninigret.

Coupled with the fact that few studies have addressed ground water transport in southern Rhode Island, two other problems are encountered in comparing investigations: 1.) length of study, and; 2.) how the term "ground water" is defined and measured. Results from this study pertain to only the summer months of 1997, and are therefore not representative of average yearly ground water fluxes to Rhode Island's salt pond region. Seasonality and annual variability with respect to water conditions must be considered if these summer values are to be compared to the annual ground water fluxes determined by Grace and Kelley (1981). In addition, "ground water", as defined by Grace and Kelley's report (1981), refers to fresh water that "either directly discharges into the ponds through the sediment, discharges through springs along the banks of the ponds, or discharges into streams which then flow into the ponds." In this study, however, no differentiation is made between stream water flowing into the ponds and the ground water which discharges into the streams; once fresh water enters the stream, it is considered stream water that eventually enters the pond. The nature of the ^{226}Ra approach implies that ground water measurements determined by this investigation include only that fresh water discharging from underground springs or diffusing through the bottom sediments of the pond.

3.4.2.e Sensitivity Analysis: Pore Water Activity, Tidal Range and Residence Time

As indicated in Eq. 2.3 and 2.4, the variables of tidal range (H), residence time (τ) and ^{226}Ra pore water activity ($^{226}Ra_{PW}$) are required to calculate ground water inputs to each of the salt ponds. These variables characteristically change from one salt pond to another, and therefore require thorough examination to determine how each of these terms affect the calculated submarine ground water flux. For the salt ponds in this investigation, values of tidal range and ^{226}Ra pore water activity are well-constrained from literature data or laboratory analysis performed in this study (see Table 3.1; Table 3.8). On the other hand, the residence times of the coastal ponds of southern Rhode Island are not well-constrained. A sensitivity analysis was conducted to ascertain how variations in these variables affect the calculated ground water flux (Figures 3.10-3.12[4]) and to

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[4] For Figures 3.11 and 3.12, ground water fluxes were calculated over a range of residence time and tidal range for determined values of $^{226}Ra_{ex}$ (10-60 dpm 100 L^{-1}) and a chosen constant $^{226}Ra_{PW}$ value of 0.005 dpm mL^{-1}. Similar plots were created for varying $^{226}Ra_{PW}$ activities bracketing the determined salt pond values (0.001-0.01 dpm mL^{-1}), producing similar results.

specifically determine the validity of the estimated residence time for the salt ponds (30 days ± 15 days).

The effect of varying ^{226}Ra pore water activity upon the calculated ground water flux for a range of residence time and tidal range is plotted in Figure 3.10. The $^{226}Ra_{PW}$ values in this plot bracket those constrained by ^{222}Rn-emanation (± 10%) for these salt ponds (Table 3.8, 3.9). It is evident that lower ^{226}Ra pore water activities result in greater ground water fluxes over the entire range of residence time and tidal height (Figure 3.10). In terms of the radium box model (Eq. 2.4), this translates into a larger input of lower pore water ^{226}Ra activity to balance the inferred ground water term (i.e. the difference between the export and influx of ^{226}Ra).

Ground water fluxes calculated over a range of tidal height (0-250 cm) for varying $^{226}Ra_{ex}$ (10-60 dpm 100 L^{-1}), residence time (5-100 days) and constant $^{226}Ra_{PW}$ (0.005 dpm mL^{-1}) are plotted in Figure 3.11. A direct relationship exists between tidal range and the calculated ground water flux, which is also inferred from Eq. 2.3. In addition, variations in ground water flux, as determined by Eq. 2.4, are sensitive to changes in tidal height for the range of residence time and pore water ^{226}Ra activity. Tidal range, however, is well-constrained for each of the salt ponds (Table 3.1).

The largest degree of uncertainty in the calculated ground water flux is in estimating the residence time (τ) of the salt ponds. In fact, no previous studies have quantified the residence times of these ponds. As a result, a range of residence time (30 ± 15 days) was

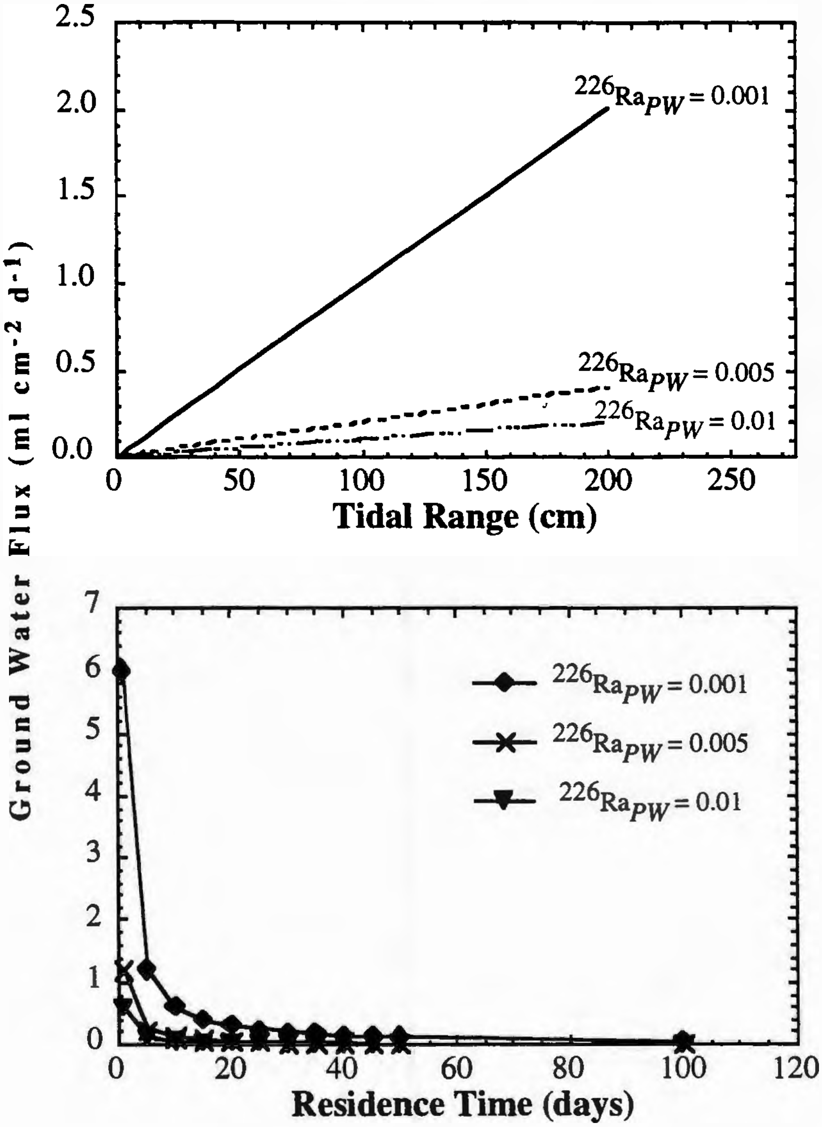

Figure 3.10 Effect of varying pore water ^{226}Ra activity ($^{226}Ra_{PW}$, dpm mL^{-1}) on the calculated ground water flux (Eq. 2.4) for salt ponds of southern Rhode Island.

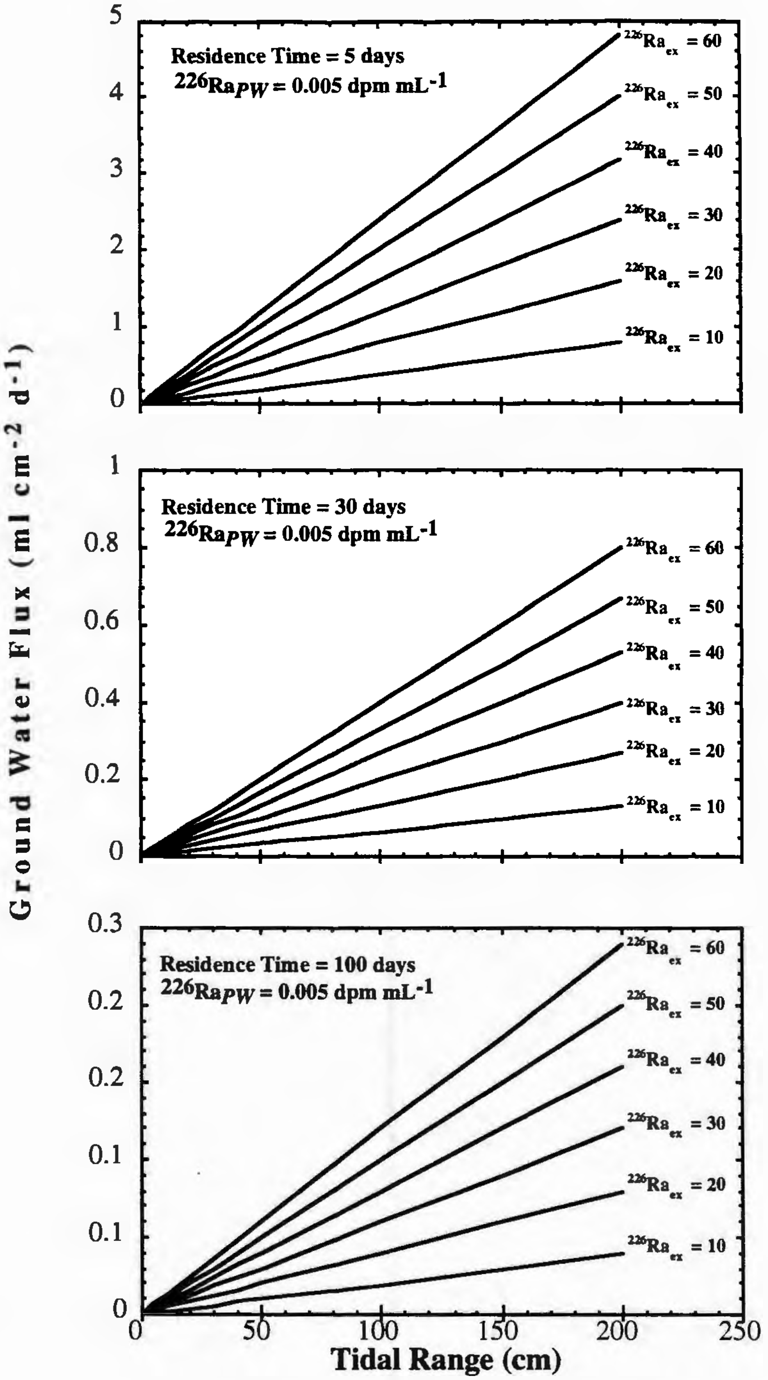

Figure 3.11 Effect of varying tidal range on the calculated ground water flux (Eq. 2.4) for salt ponds of southern Rhode Island. Units of $^{226}Ra_{ex}$ are dpm 100 L^{-1}.

used to calculate the ground water flux to each of the salt ponds (Figure 3.9). This estimated range of residence time is based on the limited research that has been done (Hinga, 1998; Olsen and Lee, 1985), for which a residence time assuming a 5% per day flushing rate ($\tau \sim 22$ days) has generally been used for the larger, more tidally-influenced ponds of Point Judith and Ninigret. The smaller ponds of Potter and Green Hill, which are not permanently connected to off-shore waters through an inlet or breachway, do not experience as much tidal flushing as the larger salt ponds, and therefore should be characterized by a longer residence time.

Figure 3.12 shows the results of a sensitivity analysis to determine the relationship between ground water flux and water residence time for values of τ considered to be representative of the salt ponds of southern Rhode Island (15-45 days). For the salt pond equations, the calculated ground water flux increases dramatically for residence times less than ~10 days, which are characteristic of more tidally-flushed systems such as the North Inlet salt marsh (Rama and Moore, 1996). Such short water residence times are most likely not representative of the salt ponds of southern Rhode Island, which experience limited tidal exchange with the adjacent shelf waters. Importantly, ground water flux values do not vary significantly over the range of residence time assumed to be representative of these coastal lagoons (15-45 days).

It should be noted that the inverse power function illustrated in Figure 3.12 is an inherent artifact of the total ^{226}Ra export equation (Eq. 2.3), which is a term in the overall ground water flux equation for the salt ponds (Eq. 2.4). In these equations, ground water is

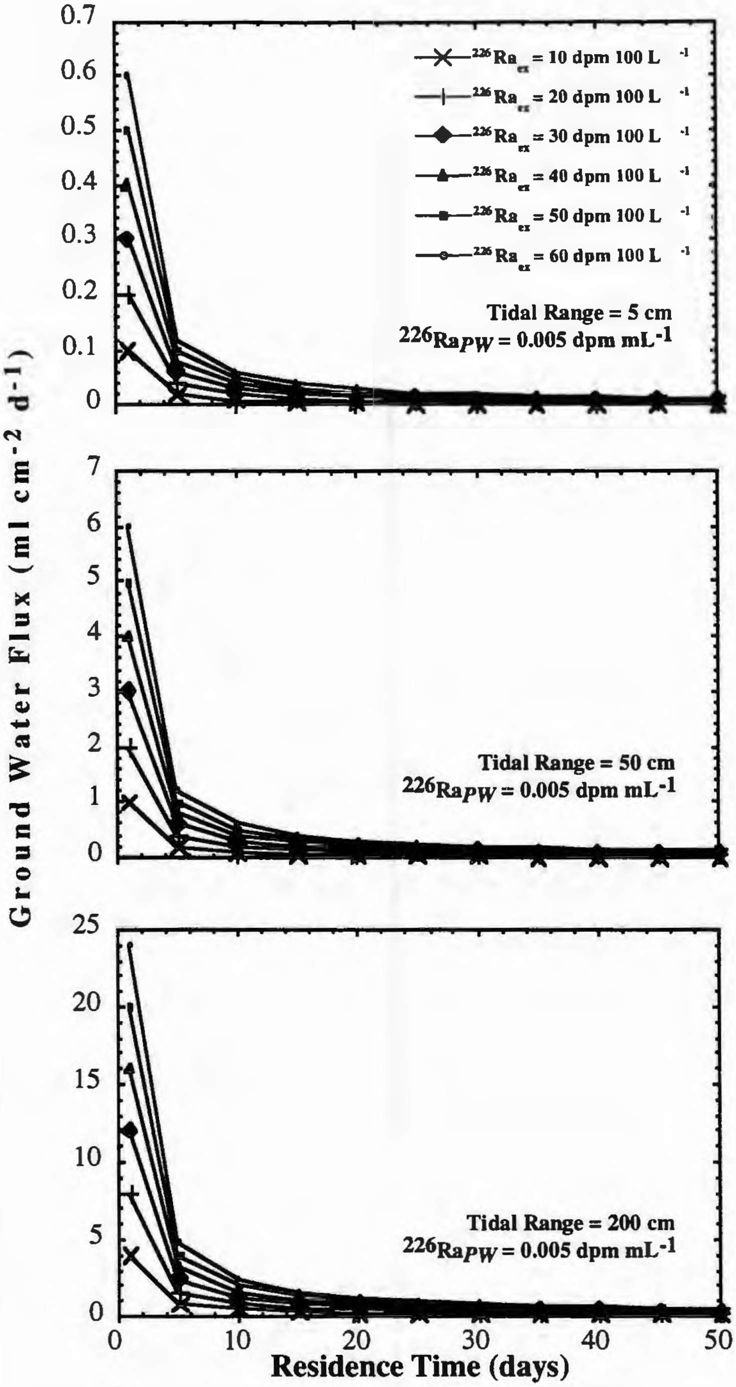

Figure 3.12 Effect of varying residence time on the calculated ground water flux (Eq. 2.4) for salt ponds of southern Rhode Island.

inversely proportional to residence time (τ), while directly related to tidal range (H). The key to the equations lies in the ratio of tidal range to residence time or the "H/τ" term. For the residence time plots, if the term "H/τ" instead of ground water is plotted against residence time, the same sloping trend is seen as that of Figure 3.12. The combined term of "H/τ" used in the residence time sensitivity analysis for the salt ponds (see Eq. 2.3; Figure 3.12) represents the ratio of a constant number (tidal range) to a varying number (residence time), and appears to govern the slope of the curve in the ground water flux calculations. For the tidal range sensitivity analysis (Figure 3.11), however, this relationship is not observed as the "H/τ" term now includes a varying number (tidal range) over a constant number (residence time), resulting in a direct, linear relation.

3.4.3 Nutrient Influx to Salt Ponds

By combining the calculated submarine ground water fluxes with the nutrient concentrations in the coastal ponds and local ground water wells, the nutrient flux to each of the salt ponds of southern Rhode Island can be evaluated (Appendix C, Table C.2). In this study, inorganic nitrogen species (NH_4^+, NO_2^-, NO_3^-) are the focus due to the fact that these nutrients, particularly nitrate, are a major concern with respect to nutrient management and eutrophication problems affecting Rhode Island's salt pond region (Ernst, 1996; Lee and Olsen, 1985; Olsen and Lee, 1985).

Inorganic nitrogen results for ground water[5] and salt pond samples collected during the summer 1997 study period are listed in Table 3.12. Salt pond concentrations range from 5-15 µM total inorganic nitrogen, with NO_2^- and NO_3^- accounting for 0.09-0.25 and 0.61-6.00 µM, respectively, and NH_4^+ dominating the overall nitrogen concentration (2.98-8.55 µM). Overall, ground water concentrations average 1.52 µM for NH_4^+, 0.075 µM for NO_2^- and 175.72 µM for NO_3^-. Compared to the salt ponds, total inorganic N concentrations in ground water in southern Rhode Island are approximately one order of magnitude greater, averaging ~177 µM nitrogen.

In a study by Olsen and Lee in 1985, nitrate was determined to be the predominant form of nitrogen in ground water for the salt pond region. Over 10 years later, results from this research provide further support for these earlier observations, with nitrate accounting for greater than 84% of the total inorganic nitrogen for all sampled ground water wells (Table 3.12). As noted above, nitrate results from this study indicate an average ground water concentration of ~176 µM. These nitrate values are slightly above the U.S. EPA drinking water health limit of 10 ppm (161 µM) (http://www.epa.gov/ogwd000/dwh/t-ioc.nitrates.html, 1998) and could potentially pose a serious health threat. However, since the given nitrate value is an average value, nitrate concentrations for individual wells

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[5] Nitrogen results are separated into three classes (i.e. all wells, medium-deep wells, and shallow surface wells) based on the source, specifically the depth, of the ground water diffusing into the salt ponds.

Table 3.12 Average and total inorganic nitrogen concentrations for measured ground water wells and salt ponds in southern Rhode Island. All units are in µM.

Ground Water Wells:	NH_4^+	NO_2^-	NO_3^-	*Total inorganic N*
Avg. well nutrient concentration (µM):				
shallow, surface wells	1.54	0.088	249.86	*251.49*
medium-deep wells	1.47	0.048	27.43	*28.95*
all wells	1.52	0.075	175.72	*177.31*

Salt Ponds:	Point Judith	Potter	Green Hill	Ninigret
Avg. salt pond nutrient concentration (µM):				
NH_4^+	4.28	4.57	8.55	2.98
NO_2^-	0.25	0.13	0.20	0.09
NO_3^-	5.76	0.61	6.00	2.22
Total inorganic N:	*10.29*	*5.31*	*14.75*	*5.29*

(Table 3.5) should be examined to determine which ground water areas need to be addressed as possible health risks.

Compared to earlier nitrate concentrations of ~20-90 μM in ground water near the Rhode Island salt pond region (Olsen and Lee, 1985), the concentrations reported in this study are one order of magnitude greater. The increase in ground water NO_3^- levels over the past decade is most likely the result of increased anthropogenic input associated with rapid development in Rhode Island's south shore area. It is important to note that all forms of combined nitrogen should be regarded as potential sources of nitrate. In this regard, elevated NH_4^+ values in the salt ponds may be the result of the decay of high levels of organic matter (see POC concentrations, Table 3.8) and fertilizer inputs from neighboring developments and farms, which represent an unconverted or un-metabolized reservoir of NO_3^- in the salt pond region.

In addition to the apparent temporal variability in nitrate concentrations, significant differences are evident for different well depths. These variations inherently provide a means of qualitatively identifying the source of ground water in southern Rhode Island. Medium and deep wells are characterized by low concentrations of NO_3^-, while shallow wells typically have higher levels of nitrate (Table 3.12). Low nitrate concentrations for the deeper wells suggest that these samples are drawing from bedrock sources of ground water that are relatively unaffected by anthropogenic sources. Surface wells exhibiting higher concentrations of nitrate, however, are sampling ground water from surficial sources such as glacial till and outwash, which are most immediately impacted by nutrient inputs. Since the salt ponds of southern Rhode Island are relatively shallow in nature (less than 2 m in depth), surficial ground water is the most likely pathway for the influx of nutrients to the ponds. Calculations estimating nutrient loadings (Appendix C, Table C.2) therefore do not use nitrogen values for medium-deep or all sampled wells, but only those for the shallow, surface wells (3-9 m), which are assumed to have nutrient concentrations that are representative of the ground water entering the ponds.

Using the shallow well nutrient concentrations and estimated ground water flows (Section 4.4.2.c), ground water nutrient influxes of NH_4^+, NO_2^- and NO_3^- to each of the salt ponds are determined. Results indicate that the majority of incoming nitrogen is in the form of nitrate, with total inorganic nitrogen flux values ranging from 0.287 kg N d^{-1} for Green Hill Pond to 14.65 kg N d^{-1} for Point Judith Pond (Table 3.13). Based on the average salt pond N concentration and calculated ground water fluxes of inorganic N, an estimate can be made of the extent of ground water input to the overall salt pond concentration. These estimates suggest that for all ponds, except Green Hill, ground water accounts for ~21-22% of the nitrogen concentration. Note that these percentages are not the result of a mass balance in which other inputs and outputs of inorganic nitrogen to the ponds are considered (i.e. atmospheric/precipitation, stream input, runoff, denitrification, etc.), but are based on a comparison of the potential ground water input to what is measured in each of the salt ponds (see Appendix C, Table C.2).

The estimated nutrient fluxes to the salt ponds determined in this study and reported by Olsen and Lee (1985) are listed in Table 3.14. Overall, results from the two investigations

Table 3.13 Estimated ground water fluxes of inorganic nitrogen to the salt ponds. The numbers in parentheses represent that percentage of the average nutrient pond concentration that can be contributed by ground water*. Details regarding calculations are given in Appendix C, Table C.2.

Ground water nutrient loading (kg N d^{-1}):	Point Judith	Potter	Green Hill	Ninigret
NH_4^+	0.090	0.008	0.002	0.025
NO_2^-	0.005	0.0005	0.0001	0.001
NO_3^-	14.55	1.29	0.285	4.02
Total inorganic N ground water flux (kg N d^{-1}):	***14.65 (21.63%)***	***1.30 (21.54%)***	***0.287 (3.36%)***	***4.05 (21.20%)***

* Ground water refers to shallow, surface well sources used to determine ground water fluxes of inorganic nitrogen to the salt ponds.

Table 3.14 Comparison of estimated inorganic nitrogen ground water fluxes to the salt ponds calculated by this study and Olsen and Lee (1985). Units are in kg N d^{-1}.

	Ground Water Inputs of Inorganic Nitrogen	
Pond	Olsen and Lee (1985)	This Study (summer 1997)
Point Judith	74.35	14.65
Potter	30.22	1.30
Green Hill	46.08	0.287
Ninigret	103.9	4.05

are different in both magnitude and observed trends between the ponds. Note that when comparing nutrient inputs from these studies, consideration must be given to variations in the duration which ground water flux, and hence nutrient flux, has been evaluated. As noted above, results from this study pertain only to the summer months of 1997, while the values of Olsen and Lee (1985) are reported on a yearly basis, and have been converted to a daily flux in this study for comparison. As ground water levels for the summer season are historically lower compared to annual averages (Section 3.4.2.c), calculated ground water inputs to the salt ponds could potentially be lower than yearly fluxes, hence resulting in the low nutrient fluxes calculated for the summer 1997 study period.

Inter-annual variability may also be important, thereby further complicating comparisons in ground water and nutrient fluxes. Also important is urban development surrounding the ponds over the past 10 years, which has contributed various nutrient supplies to each of the ponds over time. Nevertheless, the nutrient fluxes reported in this study suggest that ground water transport for the summer months of 1997 is not as large a contributor of inorganic nitrogen to the salt ponds as compared to the yearly estimates reported in 1985 by Olsen and Lee.

Chapter 4

PRINCIPLE CONCLUSIONS AND FUTURE RESEARCH

As discussed in Chapter 1, the premise for this study is founded upon recent investigations of the role of submarine ground water transport in coastal ecosystems (Moore, 1997, 1996; Rama and Moore, 1996; Simmons, 1992; Weiskel and Howes, 1992; Valiela *et al.*, 1990; Lee and Olsen, 1985; Olsen and Lee, 1985; Bokuniewicz and Zeitlin, 1980). To evaluate ground water input to the coastal zone, the scientific basis of this research is the utilization of naturally-occurring radium isotopes, particularly ^{226}Ra, as ground water tracers (Moore, 1997, 1996; Rama and Moore, 1996). Results from these investigations have provided an independent estimate of the ground water flux to coastal environments on a regional scale. In addition to providing an evaluation of the utility of ^{226}Ra as a ground water tracer in coastal waters of New England, this thesis represents one of the first attempts to quantify the input of ground water to the salt ponds of southern Rhode Island and adjacent shelf waters. The principle conclusions and implications of this work are summarized below.

4.1 Ground Water Input to Southern Rhode Island's Salt Ponds and Adjacent Shelf Waters

Result from this thesis indicate enrichments of ^{226}Ra in coastal-zone environments of southern Rhode Island, with values ranging from ~2 dpm 100 L^{-1} in the shelf waters and to ~21-45 dpm 100 L^{-1} in the coastal ponds. Application of a ^{226}Ra box model to the coastal enrichments of ^{226}Ra determined in each of these systems provided estimates of the input of ground water to both the salt ponds of southern Rhode Island and adjacent shelf waters during the summer 1997 study period.

For the coastal waters off Rhode Island, inferred ground water inputs range from 2-10 x 10^{11} L d^{-1} (± 73.95%). When compared to estimated river inputs to the shelf waters (2.66 x 10^{10} L d^{-1}), these ground water values are ~8-38 times that from riverine sources for summer 1997, suggesting that ground water is a significant source of fresh water to Rhode Island's coastal waters. The ^{226}Ra-based ground water fluxes, however, appear unrealistic in magnitude, especially in comparison to estimates of river flow for the major southern New England river basins discharging into the shelf. In addition, crude recharge calculations for the watersheds bordering Rhode Island's coastal waters, with values on the order of ~10^9 L d^{-1} (upper limit), indicate that the local ground water reservoirs are not capable of supplying the estimated ground water fluxes.

Further ground water calculations performed, in which smaller box models for the shelf waters off southern Rhode Island were considered, reveal that regardless of box size, unreasonably large ground water flows are calculated to the shelf using the radium approach of this study. However, estimated ground water fluxes, assuming any reasonable size box model, appear more justifiable if ground water ^{226}Ra activities similar to (or greater than) the elevated brackish value determined by Moore (1996) are used in the ground water calculations (i.e. ~700 dpm 100 L^{-1}). It is suggested that the limited number of wells sampled in this research, having average ground water ^{226}Ra activities ~ 60 dpm

100 L^{-1}, do not account for all ground water sources of radium in southern Rhode Island. Based on these implications, further evaluation is required to address the usefulness of radium as a ground water tracer to Rhode Island coastal waters.

For the salt ponds investigated in southern Rhode Island, ground water flows of 0.005-0.053 mL cm^{-2} d^{-1} are calculated. These ground water fluxes, corresponding to 1-42 x 10^5 L d^{-1}, are 9-37 times less than estimates of river and stream input to the ponds. The calculated ground water inputs to the salt ponds are ~3 orders of magnitude less than estimates of watershed recharge for the region immediately surrounding the salt ponds (see Section 3.4.1.e, Method 1 - Grace and Kelley, 1981; Table 3.7), indicating that local ground water reservoirs in the salt pond region are capable of supporting these ground water flows.

Compared to a previous ground water report by Grace and Kelley (1981), the ground water fluxes to the salt ponds determined in this study are lower in magnitude. Seasonal variability in river discharge and ground water flow, as well as differences in the definition of “ground water,” may explain the apparent low ground water flows to the salt ponds evaluated during this summer study. These factors help to clarify discrepancies between previous studies (Ernst, 1996; Lee and Olsen, 1985) and this work with regard to the relative importance of ground water as a source of fresh water to the salt ponds of southern Rhode Island.

Results from a sensitivity analysis, which included the variables pore water ^{226}Ra activity, tidal range and residence time, indicate that the calculated ground water fluxes for the salt pond systems are most sensitive to changes in $^{226}Ra_{PW}$ and tidal height, and for values of τ less than ~10 days. Pore water ^{226}Ra activity and tidal range are well-constrained for the Rhode Island salt ponds, and therefore do not include variations which would greatly affect the calculated ground water fluxes. Water residence time, on the other hand, is not well-known for the coastal ponds. However, since the actual residence time for the shallow, tidal-limited salt ponds in southern Rhode Island is not expected to approach that characterized by more tidally-affected coastal systems (i.e. $\tau < 10$ days), a tighter constraint of residence time for Rhode Island's coastal lagoons is not required. Based on these findings, a range of residence time indirectly constrained through the sensitivity analysis (30 ± 15 days) was used for the ground water flux calculations.

Based on the ^{226}Ra-derived ground water inputs to the salt ponds determined in this study, nutrient fluxes are estimated using local measurements of ground water nutrient concentrations. Based on inorganic nitrogen (nitrate) data from this work and in previous investigations (Olsen and Lee, 1985), average ground water nitrate concentrations in Rhode Island's salt pond region have apparently increased over the past decade. According to EPA drinking water guidelines, these nitrate concentrations, which average ~176 μM for all ground water wells sampled, could potentially pose a health threat in some localities. With respect to the nutrient ground water flux estimates, surface wells exhibiting higher NO_3 concentrations are assumed representative of ground water advecting into the shallow salt ponds. Based on the average total inorganic N concentration of these wells (~252 μM), estimated ground water fluxes of inorganic N of ~0.3-15 kg N d^{-1} are calculated to southern Rhode Island's salt ponds. While the average ground water nitrogen concentration has increased over the past 10 years, the estimated inorganic nitrogen fluxes into the salt ponds are less than earlier studies, presumably due to differences in calculated ground water inputs and seasonal effects.

5.2 Areas for Future Research

By its very nature, submarine ground water discharge constitutes a diffuse source of fresh water to the coastal environment. The results from this research, however, give only a preliminary evaluation of ground water inputs to Rhode Island's salt pond region and adjacent shelf waters. For example, the limited sampling over a large study area conducted in this investigation has proven valuable as an initial effort in determining the applicability of ^{226}Ra as a ground water tracer in southern Rhode Island. On the other hand, the large-scale spatial variability in ground water input may not have been fully considered. To address this issue, future ground water studies in the coastal waters of southern Rhode Island, using either the ^{226}Ra approach described in this thesis or other techniques, should include a more comprehensive sampling regime, especially with respect to Rhode Island's salt ponds. It is suggested that a future focus be made on evaluating ground water input to one pond or similar coastal aquatic system, to facilitate a more extensive spatial sampling protocol.

In a similar regard, more extensive sampling for Rhode Island's shelf waters would help in evaluating the applicability of radium as a ground water tracer in this coastal environment. In addition to performing more transects off southern Rhode Island to further determine the ^{226}Ra distribution in the region, additional wells should be sampled to better constrain the ground water ^{226}Ra activities used in the shelf water calculations, thereby addressing the "missing radium" theory in the salt pond region. Such measures are suggested in hopes of explaining the enormous ground water flows calculated to Rhode Island's shelf waters in this study.

As few ground water studies have been performed in southern Rhode Island, it is also suggested that other methods be employed to serve as a comparison against the ^{226}Ra-based ground water inputs. Traditional hydrological techniques, such as seep meters, provide an inexpensive and direct comparison. Analysis of samples for other radium isotopes, such as ^{223}Ra ($t_{1/2}$ = 11.4 days), ^{224}Ra ($t_{1/2}$ =3.66 days), ^{228}Ra ($t_{1/2}$ = 5.75 years), would also be useful in validating the ground water estimates reported in this thesis. With their wide range in half-life, measurements of these additional radium isotopes would allow submarine ground water discharge to be quantified on both short-term (days-weeks) and long-term (years) time-scales.

Finally, it is important to note that these conclusions regarding ^{226}Ra and calculated ground water fluxes to the coastal waters of southern Rhode Island pertain to only the summer months of 1997 (June-August). Seasonal and annual variability in hydrological water conditions (i.e. river discharge, ground water levels) must also be considered. In addition to the afore-mentioned suggestions, it is proposed that future sampling should be conducted on a bi-weekly to monthly basis over the course of a few years to account for these seasonal and annual signals, thus providing a more comprehensive investigation of ground water input to southern Rhode Island.

Appendix A

Energy Calibration Curves for Gamma Well Detector

As detailed in Chapter 2, this appendix consists of the gamma-spectrometry calibration curves created for ^{226}Ra analysis (Figure A.1-A.5). Each calibration curve represents a measured volume of mixed gamma standard (i.e. 2 mL, 3 mL, 4 mL, 5 mL, 6 mL). These ash volumes, when analyzed in standard counting vials for well analysis, are referred to in terms of "ash height." All ash heights are analyzed on a germanium well detector over a range of energy peaks (46.5 keV to 1333.2 keV), bracketing the energy peak used to determine ^{226}Ra (i.e. via ^{214}Pb at 351.9 keV). Tables of the specific parameters used in creating the calibration curves are also provided.

Figure A.1 Well detector calibration curve: Mixed gamma standard, 2 mL ash height

Isotope	Mass of STD added (g)	Mass of STD (g)	Certified Activity (dpm)	Decay	Fraction of Ash	Activity (dpm)	Gamma Energy	Counts/min	Bkgrd. (cpm)	Branching Ratio (%)	Efficiency (%)
Pb-210	0.094	106.0195	3103560	0.97226629	0.157063	420.20567	46.5	8.359602142	0.0509935	4.5	43.939375
Th-234			1342	1	0.157063	210.77881	63.5	5.990818669	0.0509935	3.9	72.257362
Cd-109	0.094	106.0195	4992780	0.6094416	0.157063	423.7318	88.2	10.99923489	0.0489538	3.6	71.78467
Co-57	0.094	106.0195	111000	0.43047091	0.157063	6.654008	122.1	4.067329763	0.0458942	85.9	70.356566
Ce-139	0.094	106.0195	175380	0.18930816	0.157063	4.6234475	166	1.17061974	0.0428346	79.9	30.529077
Sn-113	0.094	106.0195	295260	0.13662888	0.157063	5.6177661	392	0.85386381	0.0152981	64	23.323488
Cs-137	0.094	106.0195	142080	0.97929631	0.157063	19.375977	662	2.345830145	0.0101987	85.2	14.148198
Co-60	0.094	106.0195	222000	0.88775156	0.157063	27.444856	1174.1	1.211935731	0.0050994	99.9	4.4017153
Co-60	0.094	106.0195	222000	0.88775156	0.157063	27.444856	1333.2	1.248661056	0.0050994	99.9	4.5356642

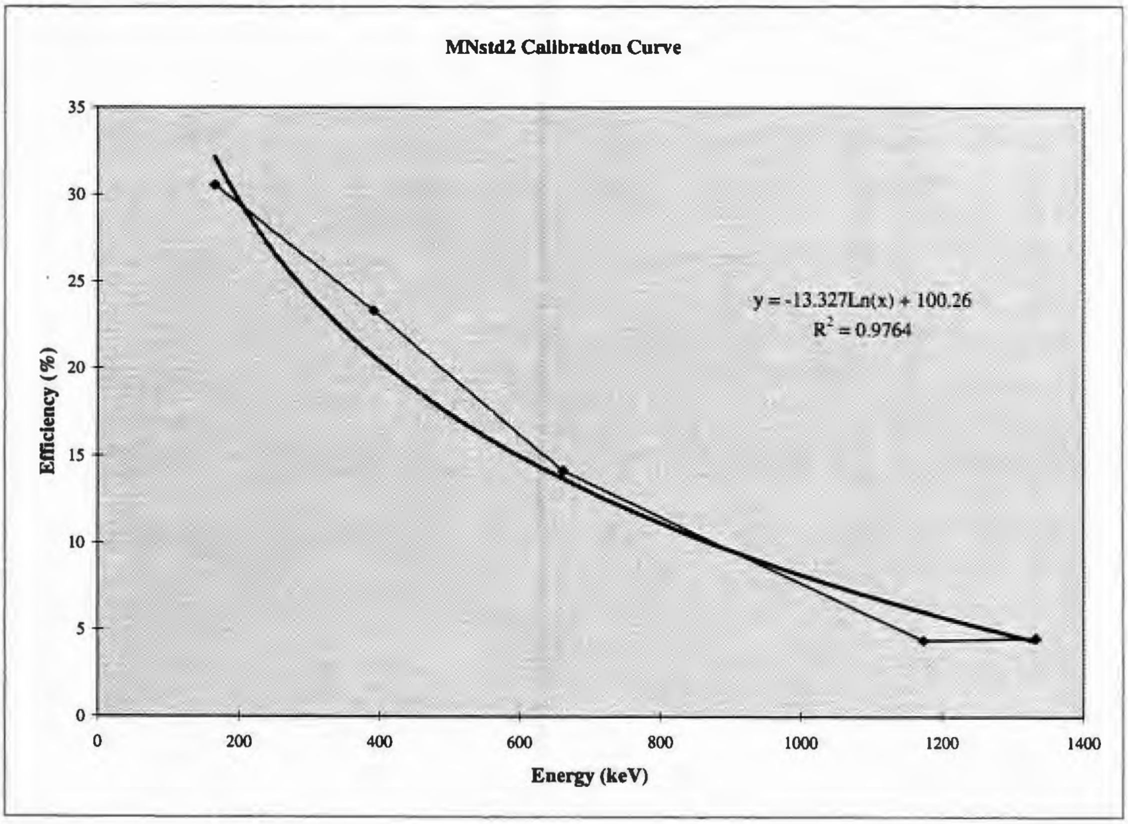


Figure A.2 Well detector calibration curve: Mixed gamma standard, 3 mL ash height

Isotope	Mass of STD added (g)	Mass of STD (g)	Certified Activity (dpm)	Decay	Fraction of Ash	Activity (dpm)	Gamma Energy	Counts/min	Bkgrd. (cpm)	Branching Ratio (%)	Efficiency (%)
Pb-210	0.094	106.0195	3103560	0.9722663	0.2314126	619.1196	46.5	11.41726832	0.0509935	4.5	40.797268
Th-234			1342	1	0.2314126	310.55576	63.2	7.595687865	0.0509935	3.9	62.292742
Cd-109	0.094	106.0195	4992780	0.6094416	0.2314126	624.3149	88.2	14.43774107	0.0489538	3.6	64.020342
Co-57	0.094	106.0195	111000	0.4304709	0.2314126	9.8038343	122.1	5.334783899	0.0458942	85.9	62.802277
Ce-139	0.094	106.0195	175380	0.1893082	0.2314126	6.8120617	166	1.697161507	0.0428346	79.9	30.394569
Sn-113	0.094	106.0195	295260	0.1366289	0.2314126	8.2770636	392.1	1.115616655	0.0152981	64	20.771229
Cs-137	0.094	106.0195	142080	0.9792963	0.2314126	28.548037	662.1	2.486400949	0.0101987	85.2	10.180527
Co-60	0.094	106.0195	222000	0.8877516	0.2314126	40.436504	1174.1	1.596281278	0.0050994	99.9	3.9389526
Co-60	0.094	106.0195	222000	0.8877516	0.2314126	40.436504	1333.7	1.459796261	0.0050994	99.9	3.6010855

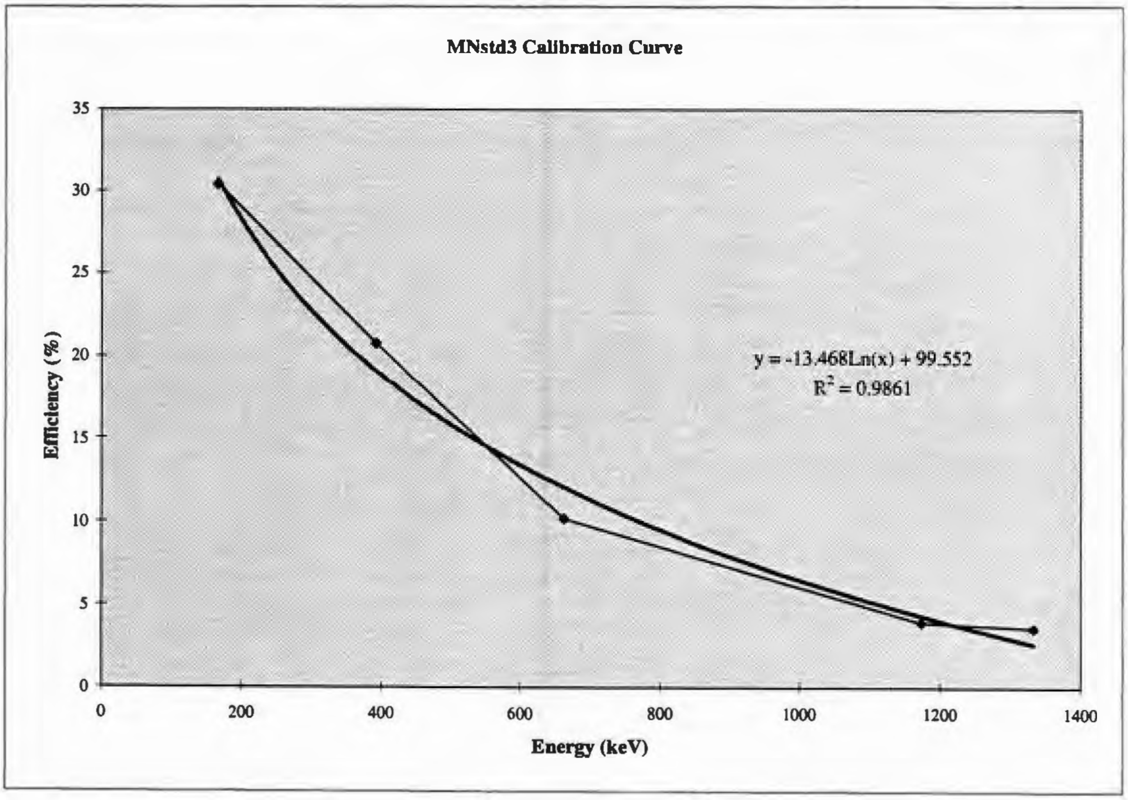


Figure A.3 Well detector calibration curve: Mixed gamma standard, 4 mL ash height

Isotope	Mass of STD added (g)	Mass of STD (g)	Certified Activity (dpm)	Decay	Fraction of Ash	Activity (dpm)	Gamma Energy	Counts/min	Bkgrd. (cpm)	Branching Ratio (%)	Efficiency (%)
Pb-210	0.094	106.0195	3103560	0.9722663	0.330855	885.16698	46.5	13.9795047	0.0509935	4.5	34.967693
Th-234			1342	1	0.330855	444.00743	63.5	9.75234842	0.0509935	3.9	56.024442
Cd-109	0.094	106.0195	4992780	0.6094416	0.330855	892.5948	88.2	18.57386849	0.0489538	3.6	57.650007
Co-57	0.094	106.0195	111000	0.4304709	0.330855	14.016727	122.3	6.857386849	0.0458942	85.9	56.572128
Ce-139	0.094	106.0195	175380	0.1893082	0.330855	9.7393332	166	2.365499573	0.0428346	79.9	29.84768
Sn-113	0.094	106.0195	295260	0.1366289	0.330855	11.833874	392.1	1.426131512	0.0152981	64	18.628112
Cs-137	0.094	106.0195	142080	0.9792963	0.330855	40.815667	662.1	3.543979505	0.0101987	85.2	10.161858
Co-60	0.094	106.0195	222000	0.8877516	0.330855	57.812833	1174.1	2.177625961	0.0050994	99.9	3.7616239
Co-60	0.094	106.0195	222000	0.8877516	0.330855	57.812833	1333.5	1.502988898	0.0050994	99.9	2.5935227

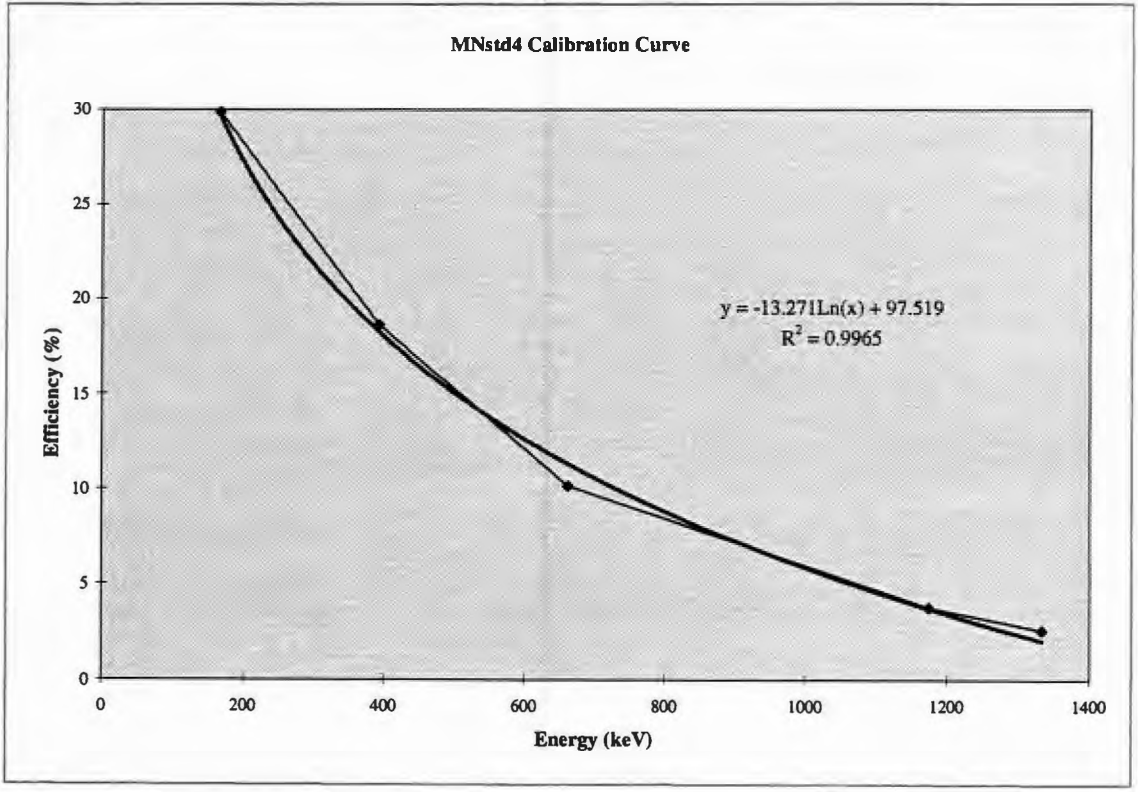


Figure A.4 Well detector calibration curve: Mixed gamma standard, 5 mL ash height

Isotope	Mass of STD added (g)	Mass of STD (g)	Certified Activity (dpm)	Decay	Fraction of Ash	Activity (dpm)	Gamma Energy	Counts/min	Bkgrd. (cpm)	Branching Ratio (%)	Efficiency (%)
Pb-210	0.094	106.0195	3103560	0.9722663	0.4089219	1094.0266	46.5	15.27272727	0.0509935	4.5	30.918878
Th-234			1342	1	0.4089219	548.77323	63.5	8.848484848	0.0509935	3.9	41.105631
Cd-109	0.094	106.0195	4992780	0.6094416	0.4089219	1103.2071	88	19.29004329	0.0489538	3.6	48.447361
Co-57	0.094	106.0195	111000	0.4304709	0.4089219	17.324044	122.1	5.714285714	0.0458942	85.9	38.090563
Ce-139	0.094	106.0195	175380	0.1893082	0.4089219	12.037378	165.8	2.285714286	0.0428346	79.9	23.319933
Sn-113	0.094	106.0195	295260	0.1366289	0.4089219	14.626137	392.3	1.523809524	0.0152981	64	16.115323
Cs-137	0.094	106.0195	142080	0.9792963	0.4089219	50.44633	662.1	3.116883117	0.0101987	85.2	7.2281635
Co-60	0.094	106.0195	222000	0.8877516	0.4089219	71.454063	1173.8	2.891774892	0.0050994	99.9	4.043948
Co-60	0.094	106.0195	222000	0.8877516	0.4089219	71.454063	1333.2	2.251082251	0.0050994	99.9	3.1464007

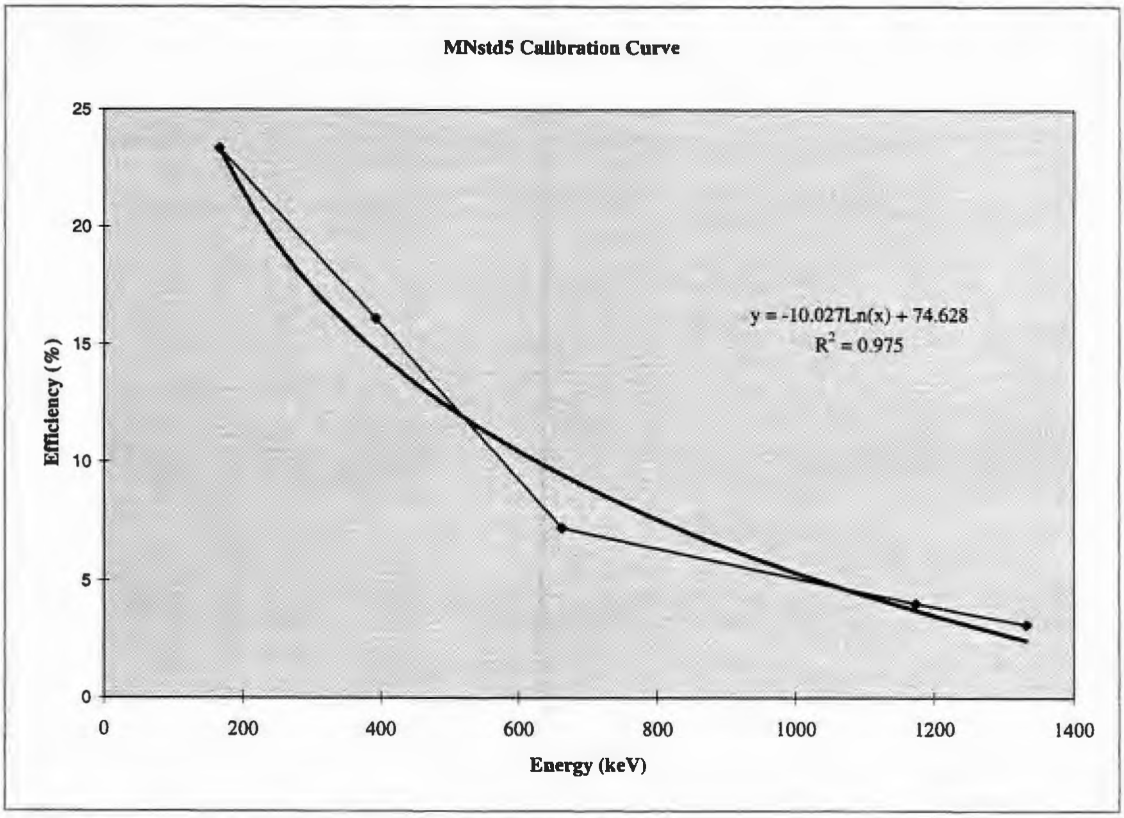
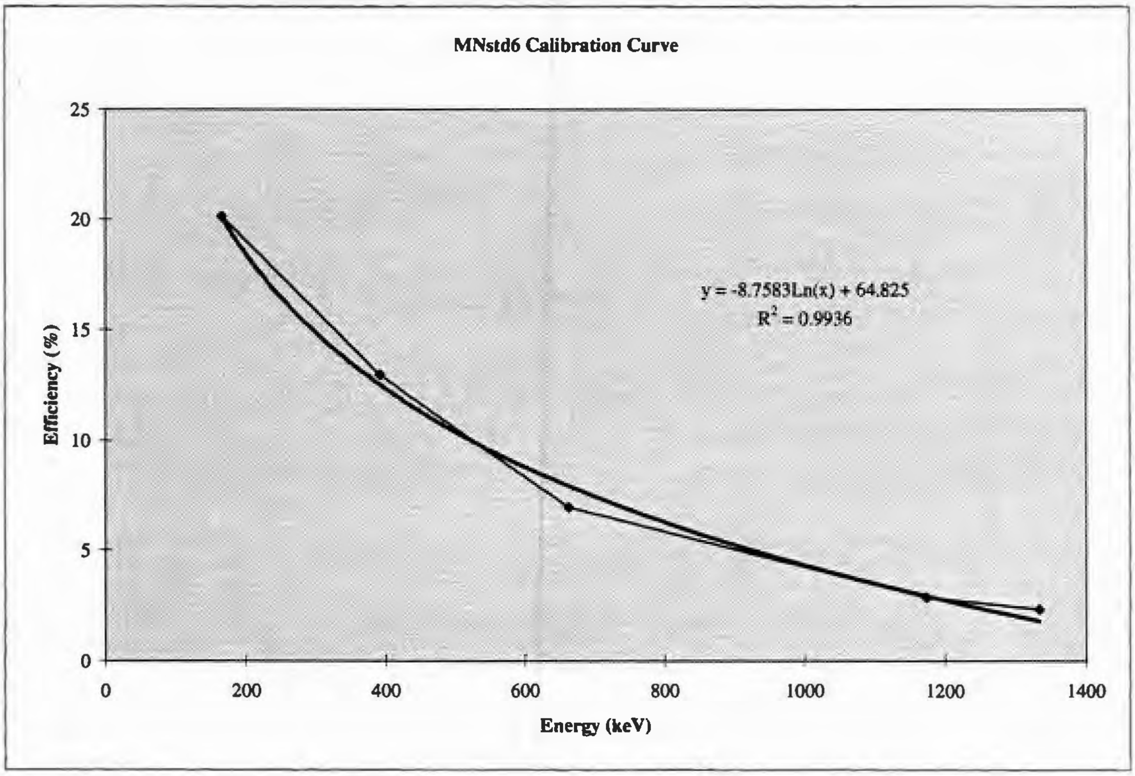


Figure A.5 Well detector calibration curve: Mixed gamma standard, 6 mL ash height

Isotope	Mass of STD added (g)	Mass of STD (g)	Certified Activity (dpm)	Decay	Fraction of Ash	Activity (dpm)	Gamma Energy	Counts/min	Bkgrd. (cpm)	Branching Ratio (%)	Efficiency (%)
Pb-210	0.094	106.0195	3103560	0.9722663	0.4888476	1307.8591	46.5	14.68782518	0.050993524	4.5	24.869876
Th-234			1342	1	0.4888476	656.03346	63.5	9.786680541	0.050993524	3.9	38.05187
Cd-109	0.094	106.0195	4992780	0.6094416	0.4888476	1318.8339	88.2	18.74609781	0.048953783	3.6	39.380631
Co-57	0.094	106.0195	111000	0.4304709	0.4888476	20.710108	122.1	7.055150884	0.045894171	85.9	39.40002
Ce-139	0.094	106.0195	175380	0.1893082	0.4888476	14.390138	166	2.356919875	0.04283456	79.9	20.12647
Sn-113	0.094	106.0195	295260	0.1366289	0.4888476	17.484881	391.8	1.467221644	0.015298057	64	12.974813
Cs-137	0.094	106.0195	142080	0.9792963	0.4888476	60.306294	662.1	3.582206035	0.010198705	85.2	6.9520055
Co-60	0.094	106.0195	222000	0.8877516	0.4888476	85.420084	1173.8	2.44276795	0.005099352	99.9	2.8565983
Co-60	0.094	106.0195	222000	0.8877516	0.4888476	85.420084	1333.5	1.997918835	0.005099352	99.9	2.3352989



MNstd6 Calibration Curve

Appendix B

Ground Water Calculations for Rhode Island's Shelf Water

Details concerning the ground water flux calculations for the shelf waters off southern Rhode Island are given in this appendix. Specifically, Appendix B contains calculations related to estimates of total mean river discharge to Rhode Island's shelf water and ^{226}Ra river contributions (Table B.1 and B.2, respectively), ground water flux values to the near-shore waters (Table B.3) and watershed recharge for the coastal region of southern Rhode Island (Table B.4). Uncertainties in ^{226}Ra activities and estimated shelf residence time and volume were propagated through subsequent calculations according to the equations listed in Skoog *et al.* (1992).

Table B.1 Estimated river input to southern Rhode Island shelf waters for June-August 1997. Suspended particulate matter (SPM) concentrations are indicated when available.

River	USGS Gauging Station I.D.	Discharge (L d^{-1})	SPM (mg L^{-1})
[1]*Coastal Rivers :*			
Quashnet	011058837	5.3 x 10^7	
Paskamanset	01105933	2.94 x 10^7	
Ten Mile	01109403	8.42 x 10^7	
Taunton	01108000	3.06 x 10^8	15
Blackstone	01112500	4.45 x 10^8	12
Moshassuck	01114000	3.43 x 10^7	
Woonasquatucket	01114500	4.58 x 10^7	
Pawtuxet	01116500	3.47 x 10^8	~5-10
Hunt	01117000	3.74 x 10^7	
Pawcatuck	01118500	4.58 x 10^8	5
Indian	01195100	2.70 x 106	
Connecticut	01184000	2.4 x 10^{10}*	
Yantic	01127500	6.90 x 10^7	
Little	01123000	3.2 x 10^7	
Quinebaug	01127000	6.53 x 10^8	
[2]*Salt Ponds Rivers:*			
Saugatucket		1.0 x 10^5	
Factory Pond		2.0 x 10^3	
Teal Pond		1.0 x 10^3	
Cross Mill		1.0 x 10^4	
TOTAL		***2.66 x 10^{10}***	

* Connecticut River discharge calculated by taking discharge data for upstream gauging station (01184000) and multiplying by ratio of drainage basin areas for downstream (01195100) and upstream stations, as no data available for coastal station 01195100.

Table B.1
(continued)

[1] Data obtained from "USGS Water Resources Data, 1997" for coastal rivers in southern Rhode Island, Massachusetts and Connecticut (Davies *et al.*, 1997; Socolow *et al.*, 1997). Discharge values represent average values for June-August.

[2] Data from Ernst (1996) for rivers and streams discharging into salt ponds of southern Rhode Island. Discharge data from 1995 stream survey for comparable water conditions (i.e. stream flow, ground water levels) to 1997 summer study period (http://met-www.cit.cornell.edu/Impacts.html, 1998).

Table B.2 Details concerning calculations used to estimate ^{226}Ra river contributions to Rhode Island's shelf waters. Assumptions and parameters (indicated in parentheses) are listed below.

Total ^{226}Ra Riverine Input = Sediment Input (Desorbed) + River Input (Dissolved)

Sediment Input: (1 x 2 x 3)

SPM (mg L^{-1}):	Input (dpm d^{-1})
50	2.66 x 10^{9}

River Input: (1 x 4) 1.06 x 10^{9} dpm d^{-1}

Total Riverine Input:

SPM (mg L^{-1}):	Input (dpm d^{-1})
50	3.72 x 10^{9}

^{226}Ra River Contributions: using Eq. 2.1 or $\left(\dfrac{5\times 6}{7}\right)$

SPM (mg L^{-1}):	^{226}Ra$_{river}$ (dpm 100 L^{-1})
50	0.034

---

1 Average river discharge to Rhode Island shelf waters (see Appendix B, Table B.1)

2 Desorbable ^{226}Ra = 2 dpm g^{-1} (Elsinger and Moore, 1983, 1980)

3 SPM value assumed for calculations (50 mg L^{-1}; see Section 3.4.1.c)

4 Dissolved ^{226}Ra river input = 4 dpm 100 L^{-1} (Li and Chan, 1979; Li *et al.*, 1977; see Section 3.4.1.c)

5 Total ^{226}Ra river supply (dissolved + desorbed)

6 Estimated residence time of enriched shelf (30 d; see Section 3.4.1.b)

7 Volume of enriched shelf (3.24 x 10^{14} L; see Section 3.4.1.b)

Table B.3 Calculations for determining ground water flux values to shelf waters off southern Rhode Island. Assumption and parameters (indicated in parentheses) are listed below.

$^{226}Ra_{ex}$ = activity of shelf waters - open ocean activity - desorption in estuaries

	^{226}Ra (dpm 100 L^{-1})
Average shelf activity	10.85 ± 1.11
Average open ocean activity	8.0 ± 0.5
Desorption in estuaries (max.) (Moore, 1996)	1
$^{226}Ra_{ex}$	**1.85 ± 1.22**

Ground Water Input to Shelf Waters: using Eq. 2.2 or $\left(\frac{1\times2}{3\times4}\right)$

Ground Water Well, ^{226}Ra (dpm 100 L^{-1})	Ground Water Flux (L d^{-1})
20	9.99 x 10^{11}
*60	**3.33 x 10^{11}**
100	2.00 x 10^{11}
	Error: 73.95%

1 Required excess ^{226}Ra input, $^{226}Ra_{ex}$

2 Volume of enriched shelf (3.24 x 10^{14} L; see Section 3.4.1.b)

3 Estimated residence time of enriched shelf (30 d; error ~ 10%; see Section 3.4.1.b)

4 Ground water ^{226}Ra activity, with ranges from 20-100 dpm 100 L^{-1} (error = 31.82%)

* Average ground water well activity (60 dpm 100 L^{-1})

Table B.4 Watershed recharge calculations for southern Rhode Island.

Method 1: using Grace and Kelly, 1981 data

recharge rate (ft yr^{-1}):	1.31	(mean)	mixed till +outwash
	2.1	(max)	mixed till +outwash
	0.5		till

			GW(ft^3 yr^{-1})		GW (m^3 yr^{-1})	
Pond		Area (ft^2)	(mean)	(max)	(mean)	(max)
Ninigret	till + outwash	3.20E+08	4.19E+08	6.71E+08	1.19E+07	1.90E+07
Green Hill	till + outwash	1.78E+08	2.33E+08	3.73E+08	6.59E+06	1.06E+07
Potter	till + outwash	1.18E+08	1.55E+08	2.48E+08	4.38E+06	7.02E+06
Point Judith	till + outwash	1.64E+08	2.15E+08	3.44E+08	6.08E+06	9.75E+06
	till	7.09E+07	3.54E+07		1.00E+06	1.00E+06
Card	till	1.71E+07	8.54E+06		2.42E+05	2.42E+05
	moraine + outwash	3.90E+07	5.11E+07	8.19E+07	1.45E+06	2.32E+06
Trustom	till	2.46E+07	1.23E+07		3.49E+05	3.49E+05
	moraine + outwash	1.74E+07	2.28E+07	3.66E+07	6.47E+05	1.04E+06

TOTAL	(mean)	(max)
m^3 yr^{-1}	3.26E+07	5.13E+07
L d^{-1}	**8.93E+07**	**1.41E+08**

Method 2: using "Appraisal of the Ground Water Reservoir Areas in Rhode Island"

*recharge rate (ft yr^{-1}):	1.31 (mean)	mixed till +outwash
	2.1 (max)	mixed till +outwash

Area of South Coastal Area	(mi^2)	75
	(ft^2)	2.09E+09

TOTAL	(mean)	(max)
ft^3 yr^{-1}	2.74E+09	4.39E+09
L d^{-1}	**2.12E+08**	**3.41E+08**

Table B.4
(continued)

Method 3: using watershed information from USGS web pages
(http://h20-nwis.er.usgs.gov/nwis-w, 1998)

*recharge rate (ft yr^{-1}): 1.31 (mean) mixed
2.1 (max) till + outwash

Basin	Area (mi^2)	Area (ft^2)	GW(ft^3 yr^{-1}) (mean)	GW(ft^3 yr^{-1}) (max)	GW (m^3 yr^{-1}) (mean)	GW (m^3 yr^{-1}) (max)
Taunton	258	7.19E+09	9.42E+09	1.51E+10	2.67E+08	4.28E+08
Ten Mile	53.1	1.48E+09	1.94E+09	3.11E+09	5.49E+07	8.80E+07
Blackstone	416	1.16E+10	1.52E+10	2.44E+10	4.30E+08	6.90E+08
Moshassuck	23.1	6.44E+08	8.44E+08	1.35E+09	2.39E+07	3.83E+07
Woonasquatucket	38.3	1.07E+09	1.40E+09	2.24E+09	3.96E+07	6.35E+07
Pawtuxet	200	5.58E+09	7.30E+09	1.17E+10	2.07E+08	3.32E+08
Potowomut	22.9	6.38E+08	8.36E+08	1.34E+09	2.37E+07	3.80E+07
Pawcatuck	295	8.22E+09	1.08E+10	1.73E+10	3.05E+08	4.89E+08
Quashnet	2.58	7.19E+07	9.42E+07	1.51E+08	2.67E+06	4.28E+06
Slocums	26.2	7.30E+08	9.57E+08	1.53E+09	2.71E+07	4.34E+07
Thames	832.3	2.32E+10	3.04E+10	4.87E+10	8.61E+08	1.38E+09
				GW (m^3 yr^{-1})	2.24E+09	3.59E+09
				GW (L d^{-1})	**6.14E+09**	**9.84E+09**

* Watershed recharge rates (mean and maximum) from Grace and Kelley, 1981.

Note: Ground Water Recharge Rates = Aquifer Recharge Rate × Watershed Area

$$[L^3\,T^{-1}] \equiv [L\,T^{-1}] \times [L^2]$$

Appendix C

Ground Water Calculations for Salt Ponds of Southern Rhode Island

Appendix C consists of the calculations regarding ground water input and inorganic nitrogen fluxes to Point Judith Pond, Potter Pond, Green Hill Pond and Ninigret Pond of Rhode Island's coastal region. Details concerning estimates of ground water flux and inorganic nitrogen input for the summer 1997 study period are given in Tables C.1 and C.2, respectively. Uncertainties in estimated salt pond residence time and ^{226}Ra activities for the salt ponds and pore water samples were propagated through subsequent calculations following the equations listed in Skoog *et al.* (1992).

Table C.1 Details concerning ground water flux calculations to the salt ponds of southern Rhode Island, June-August, 1997.

Pond Characteristics:

Pond	*Residence Time (d)	‡Tidal Range (cm)	‡Area (x 10^6 m^2)	‡Avg. Depth (m)	‡Volume (x 10^6 m^3)	†$^{226}Ra_{PW}$ (dpm mL^{-1})
Point Judith	30	44.5	7.85	1.8	14.1	0.005
Potter	30	20	1.35	1.8	2.43	0.005
Green Hill	30	3.7	1.55	0.8	1.24	0.009
Ninigret	30	13.7	6.45	1.2	7.74	0.008

* Estimated residence time (error = ± 50% or 15 d; see Section 3.4.2.e)
‡ Lee and Olsen, 1985
† Refers to ^{226}Ra pore water activity (error = 10%)

^{226}Ra Stream Contributions: $\left(\frac{1\times 2}{3}\right)$

Pond	Inflow Streams	Stream Flow (m^3 d^{-1})	Total Avg. Stream Input (m^3 d^{-1})	Assumed SPM (mg L^{-1})	^{226}Ra Sediment Input (dpm d^{-1})	^{226}Ra Dissolved Input (dpm d^{-1})	Total ^{226}Ra Stream Input (dpm 100 L^{-1})
Point Judith	Saugatucket River	10^5	10^5	5	10^6	4.0x10^6	1.06
Potter	none	--	--	--	--	--	--
Green Hill	Factory Pond Steam, Teal Pond Stream	2.0x10^3 10^3	6.0x10^3	2	2.4x10^4	2.4x10^5	0.64
Ninigret	Cross Mills Stream	10^4	10^4	3	6.0x10^4	4.0x10^5	0.18
TOTAL			1.13x10^5	10	1.084x10^6	4.64x10^6	1.88

Table C.1
(continued)

1 Total ^{226}Ra stream input = sediment input + dissolved river input (following same assumptions as Appendix B, Table B.2)
2 Estimated residence time of salt pond (30 d; see Section 3.4.2.e)
3 Volume of salt pond (see "Pond Characteristics" table above)

Excess ^{226}Ra :

$^{226}Ra_{ex}$ = avg. activity of salt pond - shelf activity

$^{226}Ra_{ex,F}$ (excess ^{226}Ra flux) calculated using Eq. 2.3 or $\left(\frac{4\times5}{6}\right)$

Pond	Avg. ^{226}Ra of Salt Pond (dpm 100 L^{-1})	Avg. ^{226}Ra of Shelf (dpm 100 L^{-1})	$^{226}Ra_{ex}$ (dpm 100 L^{-1})	^{226}Ra Stream (dpm cm^{-2} d^{-1})	$^{226}Ra_{ex,F}$ (dpm cm^{-2} d^{-1})
Point Judith	33.50	11	22.17	6.37×10^{-5}	3.29×10^{-4}
Potter	31.78	11	20.45	0.0	1.36×10^{-4}
Green Hill	56.59	11	45.26	8.52×10^{-6}	5.58×10^{-5}
Ninigret	44.18	11	32.85	7.13×10^{-6}	1.50×10^{-4}

4 $^{226}Ra_{ex}$ (dpm 100 L^{-1})
5 Tidal range (see "Pond Characteristics" table above)
6 Estimated residence time of salt pond (30 d; see Section 3.4.2.e)

Total Influx:

$^{226}Ra_{influx}$ = ^{226}Ra stream + sediment-supported ^{226}Ra + pore water diffusion influx

Pond	^{226}Ra Stream (dpm cm^{-2} d^{-1})	∞sediment-supported ^{226}Ra (dpm g^{-1})	∞PW diffusion influx (dpm cm^{-2} d^{-1})	Total Influx, $^{226}Ra_{influx}$ (dpm cm^{-2} d^{-1})
Point Judith	6.37×10^{-5}	0.64	nil	6.37×10^{-5}
Potter	0.0	0.24	nil	0.0
Green Hill	8.52×10^{-6}	0.32	nil	8.52×10^{-6}
Ninigret	7.13×10^{-6}	0.68	nil	7.13×10^{-6}

∞ Neglected in determining total influx (see Section 3.4.2.b)

Table C.1
(continued)

Ground Water Input to Salt Ponds: using Eq. 2.4 or $\left(\frac{7-8}{9}\right)$

Pond	G_f (ml cm^{-2} d^{-1})	Error
Point Judith	0.053	79.15%
Potter	0.027	70.87%
Green Hill	0.005	72.44%
Ninigret	0.018	81.79%

7 $^{226}Ra_{ex,F}$ (dpm cm^{-2} d^{-1})
8 $^{226}Ra_{influx}$ (dpm cm^{-2} d^{-1})
9 $^{226}Ra_{PW}$ (dpm mL^{-1})

Table C.2 Details concerning calculations used to estimate ground water inorganic nitrogen influxes to the salt ponds of southern Rhode Island. Parameters (parentheses) are listed below.

Salt Ponds:

Pond	Average Nutrient Concentrations (µM) NH_4^+	NO_2^-	NO_3^-	Total N
Point Judith	4.28	0.25	5.76	10.29
Potter	4.57	0.13	0.61	5.30
Green Hill	8.55	0.20	6.00	14.75
Ninigret	2.98	0.09	2.22	5.29

Nitrogen content of salt ponds: kg N d^{-1} or $\left(\frac{1 \times 2 \times 3}{4}\right)$

Pond	NH_4^+	NO_2^-	NO_3^-	Total N
Point Judith	28.16	1.63	37.92	67.71
Potter	5.18	0.143	0.694	6.02
Green Hill	4.95	0.113	3.47	8.54
Ninigret	10.75	0.328	8.02	19.10

1 Nutrient concentration of salt pond (µM or µmol L^{-1})
2 Molecular weight of nitrogen (~14 g mol^{-1})
3 Estimated volume of salt pond (see Chapter 3, Table 3.1)
4 Estimated residence time of salt pond (30 days; Section 3.4.2.e)

Ground Water:

Nutrient	Average Concentration in Shallow Wells (µM)
NH_4^+	1.54
NO_2^-	249.86
NO_3^-	0.088
Total Inorganic N	251.49

Table C.2
(continued)

Nitrogen input to salt ponds from ground water flow: kg N d^{-1} or $(5 \times 6 \times 7)$

Pond	Ground Water Input (L d^{-1})	Ground Water Nitrogen Influx NH_4^+	NO_2^-	NO_3^-	Total Inorganic N
Point Judith	4.16×10^6	0.090	0.005	14.55	14.65
Potter	3.68×10^5	0.008	0.0005	1.29	1.30
Green Hill	8.15×10^4	0.002	0.0001	0.285	0.287
Ninigret	1.15×10^6	0.025	0.001	4.02	4.05

5 Nutrient concentration of shallow ground water wells (μM or μmol L^{-1})
6 Molecular Weight of nitrogen (~14 g mol^{-1})
7 Estimated ground water flux to salt pond (column 2; L d^{-1})

Nutrient Comparison of Ground Water Contributions to Salt Pond Content:

% represents ratio of ground water nutrient influx to salt pond content

Pond	NH_4^+	NO_2^-	NO_3^-	*Total N*
Point Judith	0.32%	0.32%	38.37%	*21.63%*
Potter	0.15%	0.32%	185.53%	*21.54%*
Green Hill	0.04%	0.09%	8.21%	*3.36%*
Ninigret	0.23%	0.43%	50.17%	*21.20%*

Appendix D

^{226}Ra-based Estimates of Ground Water Input to the Gulf of Maine and Scotian Shelf

Introduction

The primary focus of this thesis is to evaluate ground water fluxes to the coastal ponds of southern Rhode Island's salt pond region and adjacent shelf waters. In addition, research was performed to evaluate inputs of ground water to the coastal waters of the Gulf of Maine and Scotian Shelf by using ^{226}Ra measurements and a simple box model. Results presented here represent a preliminary study of ground water input to the Gulf of Maine and Scotian Shelf; further research is required to better constrain the distribution of radium in this shelf water region. Results from this study indicate the potential of radium as a ground water tracer in coastal waters of the Gulf of Maine and Scotian Shelf, and provide a basis for future ground water research in this region.

Methods and Materials

Study Area

The Gulf of Maine region comprises an area of 90,700 km^2, extending 416 km from Cape Ann to Cape Sable Island and stretching 235 km lengthwise from Mt. Desert Island to the 90 meter depth off the northern edge of Georges Bank (Apollonio, 1979) (Figure D.1). The Gulf of Maine watershed covers an equally extensive area, encompassing 179,000 km^2 over three states and three Canadian provinces (http://www-

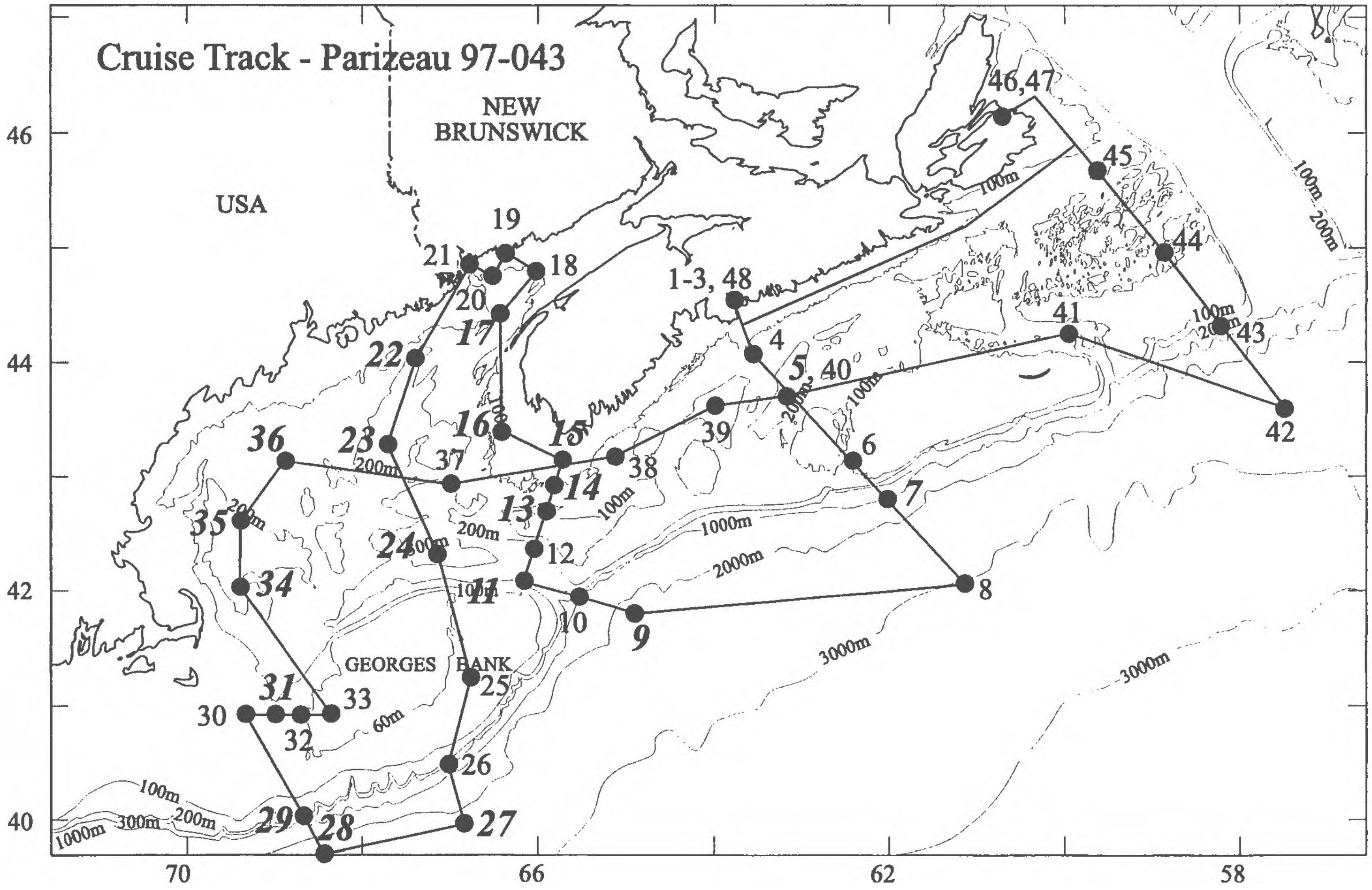


Figure D.1 Map of study area and cruise track for Gulf of Maine and Scotian Shelf, September 1997. Stations in ***italics*** represent surface seawater locations (19) sampled in this study.

orca.nos.noaa.gov/projects/gomaine, 1998). The submarine banks on its seaward edge separate the Gulf from the North Atlantic, resulting in the massive body of water to be considered a partially-enclosed sea. Surface water circulation within the Gulf tends to follow a counter-clockwise pattern, affected largely by seasonal changes in fresh water runoff and strong diurnal tides (Apollonio, 1979).

The Scotian Shelf is located adjacent to the Gulf of Maine, along the eastern coast of Nova Scotia. Seawater in the Scotian Shelf is typically defined as "a mixture of low salinity Gulf of St. Lawrence water and Slope water, which is in turn a combination of Gulf Stream water, North Atlantic Central water and Labrador Current water" (Drinkwater *et al.*, 1979). The economic importance of the Scotian Shelf lies heavily in its huge potential for gas and oil development (http://www-agc.bio.ns.ca/ndgdl/ndgdl.html, 1998). In the context of this research, the Scotian Shelf consists of the area from the continental shelf to the 3000 meter isobath (Figure D.1).

Samples were collected at 19 stations in the Gulf of Maine and Scotian Shelf during September 1997 (Figure D.1). From each station, large-volume surface seawater samples were collected using the procedures described in Chapter 2 (Section 2.3.1). Sample collection volumes ranged from ~250-1900 L, with flow rates of ~5-12 L min^{-1}[⊕]. Surface

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[⊕] Samples obtained in the Gulf of Maine and Scotian Shelf were primarily for the investigation of thorium in seawater, requiring high flow rates and large volumes for efficient tracer collection.

water samples were analyzed by gamma spectrometry using a well detector for ^{226}Ra and ^{228}Ra, as well as by ^{222}Rn-emanation for ^{226}Ra. Salinity measurements and samples for nutrient and total organic carbon (TOC) analyses were also collected at each station. *In-situ* surface salinity values were obtained from CTD casts performed during the cruise, while nutrient analysis for inorganic N (i.e. nitrate) was performed at the Bedford Institute of Oceanography, following the same laboratory methods described in Chapter 2. TOC samples were collected and analyzed according to the procedures and methods (D. Hirschberg, analyst) detailed in Chapter 2.

Results and Discussion

Radium, salinity, TOC and nitrate results for the stations sampled in the Gulf of Maine and Scotian Shelf are listed in Table D.1. Contour plots of the distribution of ^{226}Ra and ^{228}Ra activity are illustrated in Figures D.2 and D.3, respectively. For the 19 stations sampled, surface (3 m depth) salinity appears to be relatively constant, with saline values ranging from 30.62-34.86 ppt (Table D.1). The counter-clockwise circulation and fresh water input from the St. Lawrence River appear to influence the overall salinity distribution in the region. Nitrate concentrations in the upper 20 m exhibit some variability, with the highest measurements obtained for Stations 13 and 15-22 (1.686-3.886 μM) located off the southeast tip of Nova Scotia and the mouth of the Bay of Fundy (Table D.1). Near-shore runoff and/or ground water input, capable of carrying high nitrate water, may possibly account for the nitrate distribution, as well as spatial variability in biological productivity for the stations sampled.

Table D.1 Radium (^{226}Ra, ^{228}Ra), salinity, TOC and nitrate results for surface water samples collected in the Gulf of Maine and Scotian Shelf, September 1997.

Station	^{226}Ra (dpm 100 L^{-1})	^{228}Ra (dpm 100 L^{-1})	[α]Collection Efficiency (%)	[β]Salinity (ppt)	[ε]TOC (μM)	[φ]NO_3^- (μM)
5	13.17 ± 0.99	9.94 ± 2.08	49.41	30.620	83[b]	0.168
7	10.09 ± 0.66	5.54 ± 1.03	23.27	31.850	--	0.181
9	9.99 ± 0.61	7.45 ± 1.19	24.27	31.340	--	0.249
11	9.72 ± 0.53	5.89 ± 0.94	36.54	32.600	78[d]	--
13	10.49 ± 0.76	6.51 ± 1.52	23.85	32.000	95[c]	1.686
14	16.40 ± 0.59	11.96 ± 1.11	13.88	32.060	15[c]	0.436
15	10.12 ± 0.68	8.21 ± 1.36	22.92	31.800	140[b]	3.928
16	6.52 ± 0.42	5.02 ± 0.97	47.90	31.760	85[c]	3.886
17	9.69 ± 0.57	6.95 ± 1.07	29.73	32.150	84[d]	2.478
22	14.95 ± 0.84	8.44 ± 1.57	14.64	32.990	--	3.696
23	9.20 ± 0.55	4.87 ± 0.94	26.40	32.500	116[b]	0.525
24	8.62 ± 0.54	6.14 ± 0.95	38.13	32.410	74[c]	--
27	7.43 ± 0.30	3.85 ± 0.54	39.64	34.510	--	0.219
28	9.08 ± 0.51	6.73 ± 1.12	56.33	34.310	91[a]	0.542
29	9.22 ± 0.52	4.90 ± 0.88	37.84	34.860	81[a]	0.257
31	7.87 ± 0.59	6.04 ± 1.04	40.76	33.460	78[b]	0.687
34	7.95 ± 0.59	6.83 ± 0.92	39.91	31.570	--	--
35	16.52 ± 1.07	15.25 ± 2.43	10.84	31.690	78[b]	0.485
36	9.00 ± 0.54	5.32 ± 1.04	30.64	32.460	97[a]	0.385

[α] Sample collection efficiencies based on ^{226}Ra cpm values were used for both ^{226}Ra and ^{228}Ra activities.

[β] Salinity measurements at ~3 m depth, from a CTD.

[φ] Nitrate measurements are average for top 20 m.

[ε] Total organic carbon (TOC) measurements are taken at the following depths:
a. 3 m, b. 10 m, c. 25 m, d. 50 m

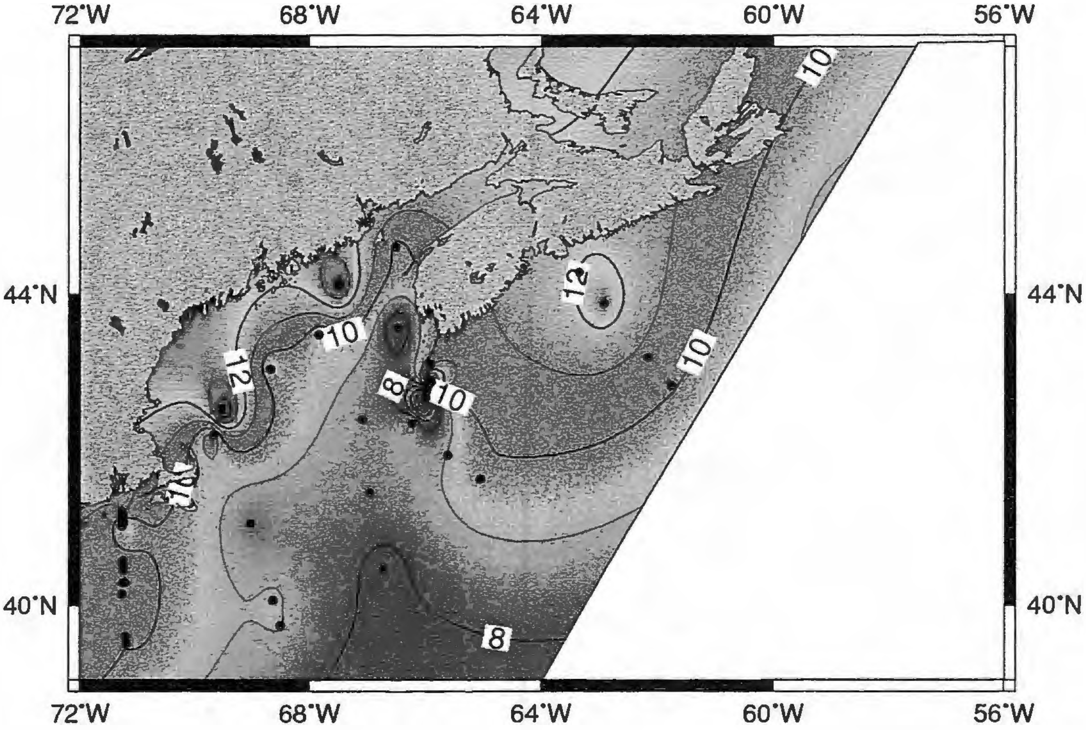

Figure D.2 Distribution of ^{226}Ra activity in surface water (3 m) in the Gulf of Maine and Scotian Shelf, September 1997. Activities are in dpm 100 L^{-1}.

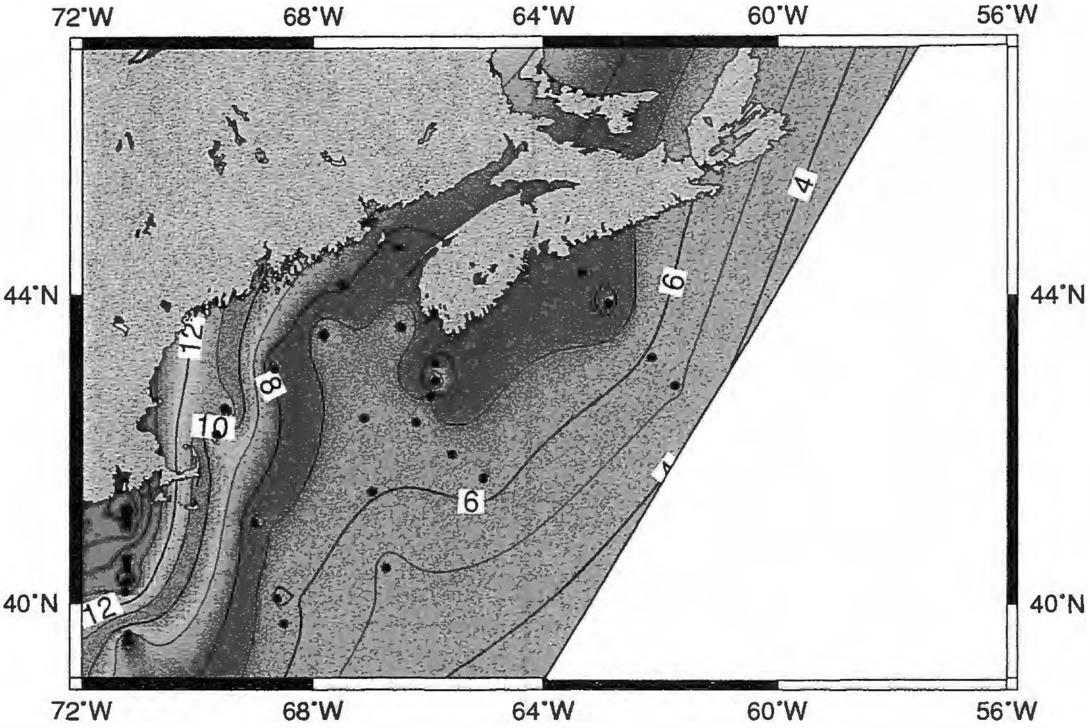

Figure D.3 Distribution of ^{228}Ra activity in surface water (3 m) in the Gulf of Maine and Scotian Shelf, September 1997. Activities are in dpm 100 L^{-1}.

For the Gulf of Maine and Scotian Shelf stations, ^{226}Ra and ^{228}Ra activities range from 6.52-16.5 dpm 100 L^{-1} and 3.85-15.3 dpm 100 L^{-1}, respectively (Table D.1; Figures D.2-3). ^{226}Ra activities are comparable to values obtained off the southern coast of Rhode Island (Section 3.3.1.a; Table 3.3, Figure 3.4), spanning a greater range of ^{226}Ra activity. Activities of ^{228}Ra determined in the Gulf of Maine and Scotian Shelf are within the range of reported values of ~5-45 dpm 100 L^{-1} for the Atlantic (Moore, 1987; Reid *et al.*, 1979; Kaufman *et al.*, 1973) and ~0.01-6.3 dpm 100 L^{-1} for the North Atlantic Ocean (Moore, 1969). The distribution of both radium isotopes suggests coastal enrichment, with near-shore waters exhibiting higher activity. The clearest sign of coastal enrichment for these radium isotopes in the Gulf of Maine and Scotian Shelf study region is observed off the eastern coast of the United States (Figures D.2-3).

Excess ^{226}Ra activities are used in the ground water flux calculations presented in this appendix. Surface ^{226}Ra enrichments are observed for the majority of stations sampled, with a few exceptions (i.e. Stations 16, 24, 27, 31 and 34). Overall, the area of Ra-enriched shelf water is approximately equal to half of the Gulf of Maine plus the entire Scotian Shelf region. As these two areas would roughly sum up to the surface area of the entire Gulf of Maine, the area dimension of the box model is approximately 1×10^{11} m^2 (Apollonio, 1979). Potential temperature results for the stations suggest a mixing depth of approximately 10-20 m (Charette, 1998). Based on these dimensions, the volume of ^{226}Ra-enriched shelf water is assumed to be $\sim 1 \times 10^{15}$ L. Estimated residence time for the Gulf of Maine and Scotian Shelf box model is assumed to be on the order of 100 days. As no residence time has been determined for this combined area, this value is assumed based on the actual τ for the entire Gulf of Maine region (~1 yr; Schlitz and Cohen, 1984) and volume transports along the Scotian Shelf (~1 x 10^5 m^3 s^{-1}; Drinkwater *et al.*, 1979; McAdie, 1994).

For the Gulf of Maine and Scotian Shelf study region, a ^{226}Ra enrichment on the order of 3 dpm 100 L^{-1} is determined using the average activity of the enriched shelf waters (~11 dpm 100 L^{-1}) and assumed open ocean ^{226}Ra value (8 dpm 100 L^{-1}; Moore, 1996). Rivers discharging in the region are not considered capable of supporting the observed ^{226}Ra excess, following the same argument presented for the Rhode Island shelf waters in Figure 3.5 (see Section 3.4.1.c). Therefore, as in the case for the Rhode Island coastal waters, additional sources of ^{226}Ra are invoked in order to support the coastal ^{226}Ra enrichment.

By applying a radium box model, an inferred submarine ground water flux of ~3-33 x 10^{10} L d^{-1} (± ~50%) is calculated for the near-shore waters of the Gulf of Maine and Scotian Shelf (Table D.2). These ground water inputs are based on a shelf ^{226}Ra enrichment of ~2 dpm 100 L^{-1} and assumed ground water well ^{226}Ra activity ranging from 60-700 dpm 100 L^{-1}. It should be noted that no measurements of ground water ^{226}Ra activity for the region surrounding the Gulf of Maine and Scotian shelf were made during this study. Instead, an assumed range of ground water ^{226}Ra activities was bracketed using the average well ^{226}Ra activity determined in southern Rhode Island (~60 dpm 100 L^{-1}) and the brackish ground water value reported by Moore (1996) for the North Inlet salt marsh (~700 dpm 100 L^{-1}).

Table D.2 Preliminary ground water flux estimates to the Gulf of Maine and Scotian Shelf study area. Assumption and parameters (indicated in parentheses) are listed below.

$^{226}\text{Ra}_{ex}$ = activity of enriched shelf waters - open ocean activity - desorption in estuaries

	^{226}Ra (dpm 100 L^{-1})
Average enriched shelf activity	11
Average open ocean activity	8
Desorption in estuaries (max.) (Moore, 1996)	1
$^{226}\text{Ra}_{ex}$	**2**

Ground Water Input to Shelf Waters: using Eq. 2.2 or $\left(\frac{1\times 2}{3\times 4}\right)$

Ground Water Well, ^{226}Ra (dpm 100 L^{-1})	Ground Water Flux (L d^{-1})	$\frac{\text{Ground Water}^{\varnothing}}{\text{River Water}}$
60	3.33×10^{11}	0.3
100	2.00×10^{11}	0.2
700	2.86×10^{10}	0.03
	(Error: ~50%)	

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1 Required excess ^{226}Ra input, $^{226}\text{Ra}_{ex}$

2 Volume of ^{226}Ra enriched shelf (~1×10^{15} L; see Results and Discussion for assumptions)

3 Estimated residence time of shelf waters (~100 days; see Results and Discussion for assumptions)

4 Ground water ^{226}Ra activity, with ranges from 60-700 dpm 100 L^{-1}

Table D.2
(continued)

∅ Ratio of estimated ground water flux to river discharge for shelf waters. River discharge determined for September 1997 period, from U.S. and Canadian Geological Survey Water Resources data for Maine, Massachusetts and Canada (http://www.maritimes.dfo.ca/cgi-test/ocean/mpbasins.pl, 1998; Nielsen *et al.*, 1997; Socolow *et al.*, 1997). Total river discharge to the region considering major river basins ~1 x 10^{12} L d^{-1}.

The calculated ground water inputs to the coastal waters of the Gulf of Maine and Scotian Shelf are approximately 1-2 orders of magnitude less than estimates of river discharge to the region (Table D.2). These preliminary results suggest that submarine ground water discharge in this study area represents a less significant component of coastal-zone fresh water input in comparison to riverine sources. Additionally, if the average ground water nitrate concentration were available for the watersheds surrounding the Gulf of Maine and Scotian Shelf, potential inorganic nutrient fluxes to the near-shore waters could be calculated based on the estimated ground water inputs.

It should be noted that the collection efficiencies of the MnO_2-impreganted cartridges used for all of the surface samples in the Gulf of Maine and Scotian Shelf are very low (less than 60%; Table D.1). These low efficiencies may be attributed to high flow rates (5-10 L min^{-1}) of the large-volume pumping procedures employed during sampling. As noted previously, samples collected in the Gulf of Maine and Scotian Shelf were collected principally for ^{234}Th analysis, for which samples can be collected at higher flow rates than for radium (1-2 L min^{-1}). As a result, it appears that these ^{226}Ra activities are affected to a certain extent by these poor collection efficiencies (Figure D.4); specifically, higher ^{226}Ra activities in the Gulf of Maine and Scotian Shelf have a tendency to be associated with lower collection efficiencies. Samples collected at optimal flow rates of 1-2 L min^{-1}, however, such as those in southern Rhode Island, indicate no dependence of collection efficiency on ^{226}Ra activity (Figure D.4, plot (b)).

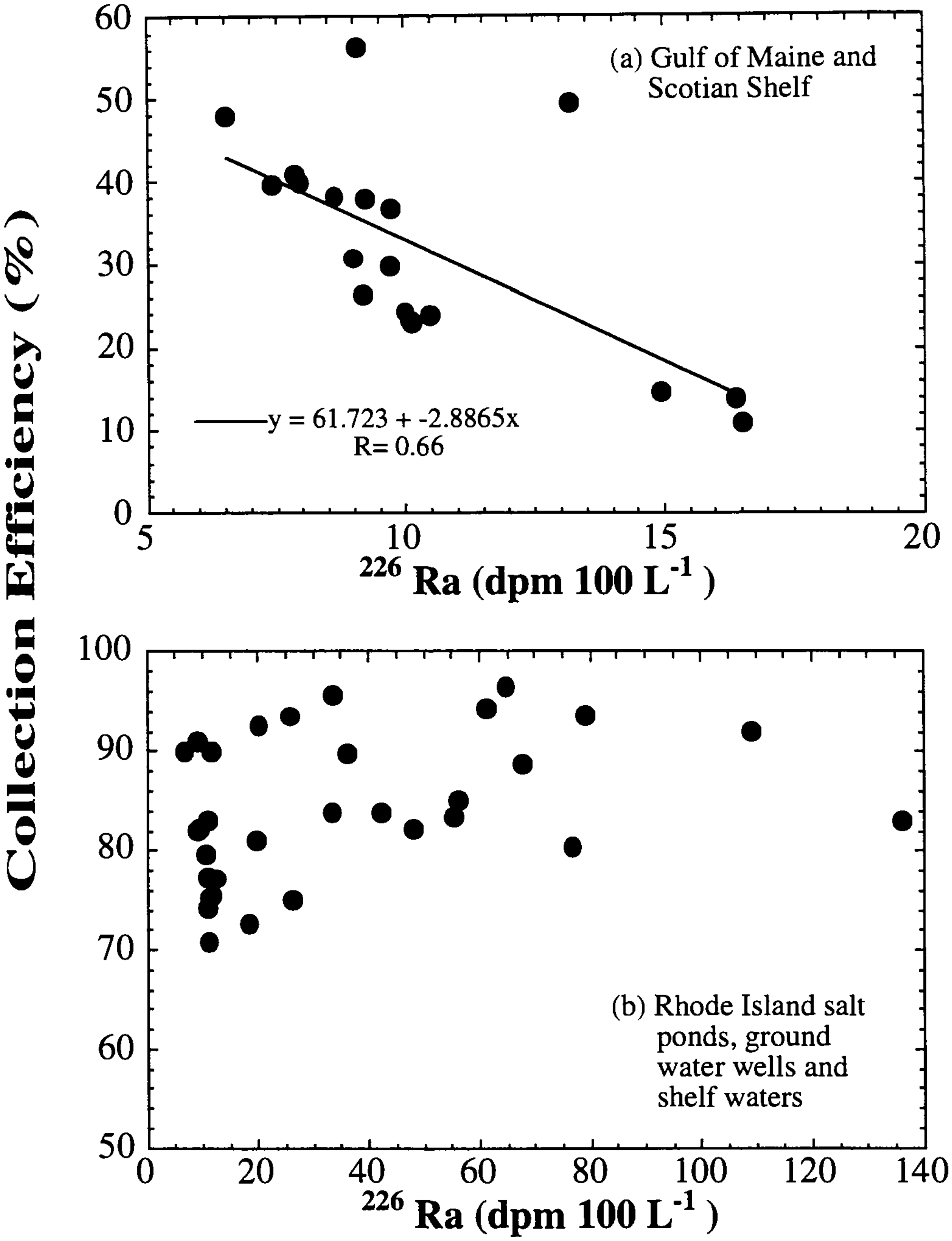

Figure D.4 MnO_2-impregnated cartridge collection efficiency plotted against ^{226}Ra activity for samples from (a) the Gulf of Maine and Scotian Shelf and (b) southern Rhode Island.

In addition, these cartridge collection efficiencies themselves have a high degree of uncertainty for radium. The Coss pumps used to sample surface waters for the Gulf of Maine and Scotian Shelf cruise often experience varying flow rates during collection. These pumps, which are lowered off the ship and therefore cannot be attended to during sample collection, tend to experience variable flow rates over time, affecting the overall collection efficiency. In addition, the cartridge efficiencies themselves may be erroneous as they are based on the assumption that any dissolved radium not scavenged on cartridge MnA is scavenged on MnB (Figure 2.1). At these higher flow rates, it is possible that water is in effect being "blasted" through the sampling system, with dissolved radium by-passing the second in-line cartridge (MnB). In other words, the "100%" collection assumption for the two cartridge system for efficient radium collection may not apply at these high flow rates.

Nevertheless, the distribution of ^{226}Ra and ^{228}Ra appears to be reasonable in the Gulf of Maine and Scotian Shelf. In particular, the near-shore ^{226}Ra enrichments of ~2-3 dpm 100 L^{-1} are similar to those obtained for the shelf waters off southern Rhode Island (Section 3.4.1). Due to the similarities in coastal enrichment between the two study areas and the reasonable radium distributions, ground water inputs to the Gulf of Maine and Scotian Shelf were calculated and presented in this appendix (Table D.2). These ground water fluxes, however, are considered to be more speculative due to the suspect nature of the presented radium activities. Moreover, given the possibility that the determined activities may in fact be high, the observed ^{226}Ra excess of ~3 dpm 100 L^{-1} in the coastal waters of the Gulf of Maine and Scotian Shelf may potentially be less, implying that the estimated ground water fluxes in this region are an upper limit. Further research is required to constrain ground water input to the region, and to better evaluate the use of radium isotopes as ground water tracers in the Gulf of Maine and Scotian Shelf.

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