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Radiochemical Estimates of Submarine Groundwater Discharge to Waquoit Bay, Massachusetts

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Submarine groundwater discharge (SGD) is the flux of fresh and brackish groundwater to the ocean through a coastal aquifer (1). Groundwater often transports large amounts of anthropogenic nitrogen and phosphorus to the ocean, and understanding the magnitude of groundwater flux is important to the environmental protection and management of coastal waters (2, 3). Recent studies have employed radium isotopes (4) and radon-222 (5), both naturally enriched in groundwater relative to surface water due to a high uranium content in aquifer sediments, to quantify SGD in coastal systems. However, these studies have been limited by a poor understanding of the distribution of these isotopes in coastal groundwater, the processes controlling these distributions, and a lack of high-resolution time-series sampling of tracer activities in surface waters. Here, we attempt to overcome these earlier limitations by mapping the distribution of ²²²Rn ($t_{1/2} = 3.83$ days) and ²²⁶Ra ($t_{1/2} = 1600$ years) across a groundwater salinity gradient, and by deploying a new *in situ* ²²²Rn analyzer to study the time dependence of SGD in Waquoit Bay.

Using a drive-point piezometer, four depth profiles of groundwater ²²⁶Ra and ²²²Rn were collected along a transect perpendicular to the shore at the head of Waquoit Bay, creating a vertical cross section of each isotope at the groundwater-seawater interface (Fig. 1). At each sampling depth, ²²⁶Ra was extracted from ~15 l of groundwater on a column of Mn-impregnated fiber. In the laboratory, the fiber was ashed and ²²⁶Ra quantified via gamma ray spectroscopy (6). For ²²²Rn, 250 ml of groundwater was collected in a glass bottle and directly analyzed on a Durrige RAD7 electronic radon monitor; activities were decay-corrected to the time of collection. To quantify tracer concentrations in surface water, discrete bay water samples for ²²⁶Ra were collected at four locations at the head of the bay. Continuous measurements of ²²²Rn at a single station at the head of Waquoit Bay were obtained using the RAD7 coupled to an air-water equilibrator as described in Burnett and Dulaiova (5). The instrument recorded the ²²²Rn activity of surface water every 30 min for 3 days. Tidal height, measured as water column depth to the sea floor at the sampling location, was monitored with a YSI 600 series CTD, and local atmospheric conditions were obtained from a nearby NOAA weather tower (# BUZM3, Buzzards Bay, MA).

²²⁶Ra activity in the groundwater increased with increasing salinity; the highest activities occurred above a salinity of 25 (Fig. 2a). The low activities (<3 dpm l⁻¹) observed at salinities of 25 or greater are from the landward portion of the transect. This is in contrast to the typical distribution of radium in estuarine surface waters, where activities are elevated at all salinities >0 and often peak at intermediate salinity (15–20) due to a desorption reaction

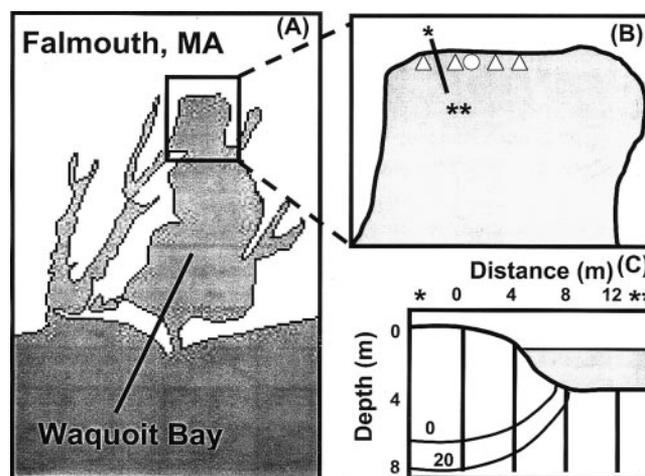


Figure 1. Location of Waquoit Bay, Massachusetts, and our sampling site during the summer of 2003. Waquoit Bay is located on the eastern border of the town of Falmouth, Massachusetts, on Cape Cod (A). Our sampling site was situated along the beach at the head of the bay (B). Surface measurements of radium-226 activity, a continuous measurement of radon-222, and a transect of four depth profiles oriented perpendicular to the beach were used to quantify SGD (B, $\Delta = ^{226}\text{Ra}$, $O = ^{222}\text{Rn}$, * - ** = transect of 4 depth profiles). A vertical cross section of groundwater revealed a sharp increase in salinity at the freshwater-saltwater interface (C, contour plot from * to **).

related to ion exchange (7). The pattern we observed could be explained by an increased ²²⁶Ra source with increasing depth and distance from shore, a function of either higher sediment content of thorium-230 (radiogenic parent of ²²⁶Ra) or a decrease in the grain size of aquifer sediments. This latter scenario would result in greater sediment surface area, thereby increasing the availability of radium for desorption. However, sediment sampling at the head of Waquoit Bay is necessary to determine which of these two possibilities is the most likely explanation for the observed pattern.

The pattern of groundwater ²²²Rn with salinity was similar to that of ²²⁶Ra, with ~3-fold increases in activity at salinities higher than 20 (Fig. 2a). ²²²Rn also displayed an increase in activity with increasing depth and distance from the berm (Fig. 2b). Because Rn is a noble gas, its distribution throughout the aquifer should be uniform, and not affected by changes in salinity. Also, because the residence time of fresh groundwater beneath the bay is several years (8), the activities of ²²²Rn in this zone are likely to be in equilibrium with the sediment activity of its parent isotope ²²⁶Ra. Therefore, the higher observed activities of ²²²Rn in the saline portion of the aquifer must be a function of a greater ²²⁶Ra source, which is consistent with the observed ²²⁶Ra distribution.

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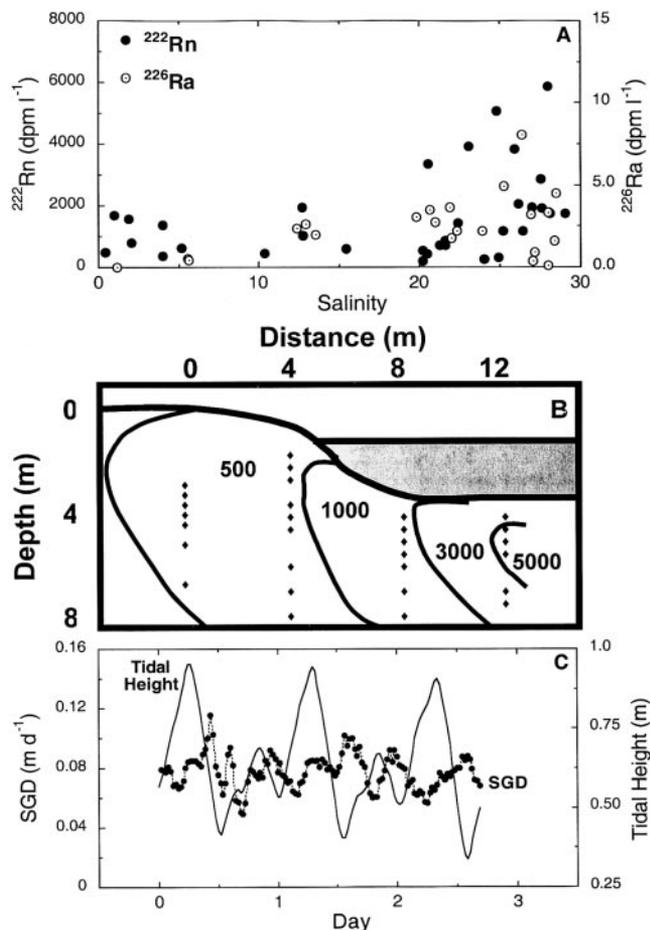


Figure 2. The distributions of radium-226 and radon-222 in groundwater displayed a pattern of increasing activity with increasing salinity, depth, and distance from the beach berm. The non-conservative distribution of ^{226}Ra and ^{222}Rn is displayed in a plot of isotope activities, measured as disintegrations per minute per liter of water (dpm l^{-1}), as a function of increasing salinity (A). A vertical cross section of ^{222}Rn activities through the fresh, intermediate, and saline portions of the aquifer (B, contour plot, individual samples represented by diamonds (\blacklozenge)) reveals increasing activity from the surface to 8 m, and distance from the berm to 12 m. A 5-point running average of the time-series record of groundwater velocities is plotted alongside tidal height above sea floor (C).

To quantify SGD to Waquoit Bay, we applied a non-steady-state mass balance model to our time-series ^{222}Rn record collected over 3 days at the head of the bay. Corrections for atmospheric evasion, loss due to advection to the lower bay, and changes in inventory due to water column depth were all applied to the time-series data using the approach of Burnett and Dulaiova (5) to calculate the excess ^{222}Rn flux ($\text{dpm m}^{-2} \text{d}^{-1}$) during each 30-min interval. Dividing by the average groundwater ^{222}Rn activity (dpm m^{-3}), we estimated SGD rates ranging from 0 to 0.16 m d^{-1} , with a mean of $0.08 \pm 0.02 \text{ m d}^{-1}$ ($n = 132, 1-\sigma$). In general, SGD was related to tidal stage (Fig. 2c), whereby SGD was highest at low tide and lowest at high tide, a result consistent with other time-

series estimates of SGD in coastal systems (6, 9). We suggest that both a change in hydraulic head gradient, modulated by the rise and fall of the tide, and the effects of subsurface recirculation due to tidal pumping are the likely explanation for this observation.

To calculate a volumetric flux of SGD ($\text{m}^3 \text{d}^{-1}$), we must first estimate the area of the seepage face at the head of Waquoit Bay. The length of the seepage face (1760 m) was obtained from a false-color aerial infrared image (1-m resolution) taken at low tide in the fall of 2002 (Charette, unpubl. data). A seepage meter study by Michael *et al.* (10) found the width of the seepage face to be 70 m. Based on this effective seepage surface area of $123,200 \text{ m}^2$, we estimated a volume discharge of $9900 \text{ m}^3 \text{d}^{-1}$. Following the mass balance model of Charette *et al.* (4) and using the same effective seepage area, we estimated a ^{226}Ra -derived volumetric flux of SGD of $\sim 1200 \text{ m}^3 \text{d}^{-1}$ ($n = 4$). Since high levels of ^{226}Ra are present only in the saline portion of the aquifer and ^{222}Rn is high in both fresh and saline groundwater (relative to surface waters), it is possible that the difference between these two estimates represents the fresh component of SGD. However, an alternative explanation is greater uncertainty in the ^{226}Ra estimate due to the limited data compared to the ^{222}Rn record.

Recent applications of ^{222}Rn and ^{226}Ra to estimate SGD have assumed that groundwater discharge is static over time and space. The flux estimate derived from the continuous ^{222}Rn record, however, suggests substantial temporal variability in groundwater discharge across a tidal cycle. This method would be useful for longer-term studies, where variability in SGD may be driven by the spring/neap tidal cycle and seasonal to interannual changes in aquifer recharge. Also, high-resolution sampling (cm scale) of ^{222}Rn and ^{226}Ra in groundwater revealed that these isotopes do not behave as predicted across a salinity gradient, probably because of an increased source term across the freshwater-saltwater interface.

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