PORE WATER RADIONUCLIDE VARIABILITY IN SMITHTOWN BAY – IMPLICATIONS FOR SUBMARINE GROUNDWATER DISCHARGE

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Submarine groundwater discharge (SGD) is an important component of the hydrologic cycle, in which both fresh (meteoric) groundwater and recirculated seawater is discharged to coastal water bodies (Moore, 1996). SGD can carry significant nutrients, trace metals, rare earth elements, and radionuclides into the coastal ocean, thus, SGD needs to be accurately quantified to estimate groundwater derived chemical loads. Radionuclide mass balance modeling (^{222}Rn and ^{223,224,226,228}Ra) is a useful method for quantifying both fresh and recirculated SGD (Burnett et al., 2006). In order to calculate SGD *via* radionuclide mass balance modeling, the radionuclide activity of the groundwater endmember must be well constrained. We find spatially and temporally variable ^{222}Rn pore water activities over a 6 month period from July – December 2014.

The difficulty of quantifying the groundwater endmember is a result of varying hydrogeologic conditions and geochemical gradients within the subterranean estuary (STE), a dynamic coastal mixing zone between fresh groundwater and recirculated seawater. Geochemical gradients and seasonal oscillations of the water table may change the sediment-bound radium activity within the STE (Gonneea et al., 2013), which in turn affects the local alpha-recoil production of ^{222}Rn.

This study investigates radionuclide variability within the STE by sampling a transect of intertidal multi-level wells at two distinct study sites. Callahan's Beach is a site of prominent freshwater discharge and was chosen to represent a typical subterranean estuary that would likely reflect changing hydrogeological conditions. Previous work has identified significant fresh SGD *via* seepage meter measurements. Fresh SGD is visibly evident at low tide along the shoreline through large rivulets. Callahan's Beach has a high hydraulic gradient, derived from steep onshore relief composed of sandy glacial outwash. Long Beach is a small barrier beach that separates Smithtown Bay from Stony Brook Harbor. Aside from a small freshwater lens, freshwater SGD at Long Beach is expected to be minimal. Thus, this location was chosen to best represent an atypical subterranean estuary that is characteristic of saline groundwater and recirculated seawater. Aside from wave and tidal changes, ^{222}Rn pore water distribution beneath Long Beach should be representative of changing biogeochemical conditions.

Callahan's Beach Results

Pore water sampled at the high tide well of Callahan's Beach was consistently fresh throughout the study period. Intertidal and low tide profile salinities varied from 0.1 – 29.94 throughout the study period, but showed consistent freshening with depth. Dissolved oxygen (DO) varied between all well profiles, however, all samples had DO >4 mg L^{-1} and were considered well oxygenated.

^{222}Rn measured within the low tide well was consistently one order of magnitude lower than activities observed up gradient in the high tide well (**Figure 1A**). Pore water ^{222}Rn distribution beneath Callahan's Beach varied monthly, however, each profile exhibited a consistent increase in ^{222}Rn activity with increasing depth. The lone exception was the deepest sample from the high tide well, which was lower in activity in comparison to the pore water sampled 1m shallower. A

^{222}Rn deficiency within the shallow portion of each profile suggests that groundwater advection is transporting ^{222}Rn rich groundwater down gradient towards the shoreline. Lower pore water salinity is consistent with greater ^{222}Rn activities (**Figure 2**).

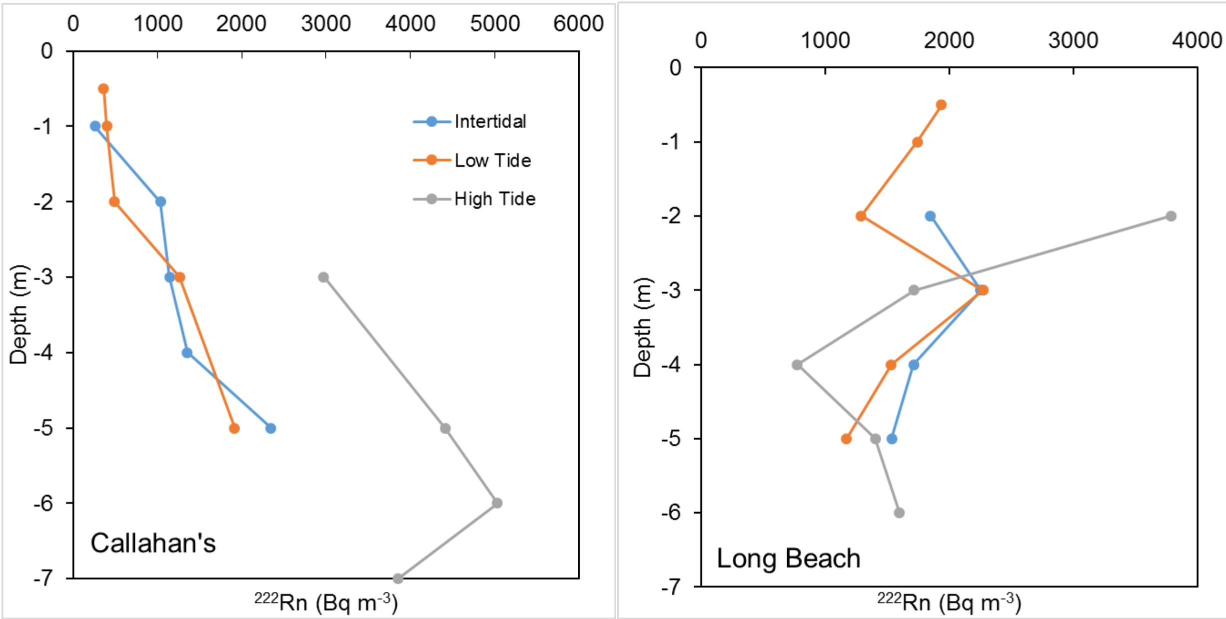

Figure 1. August 2014 ^{222}Rn pore water distribution at Callahan's Beach (A) and Long Beach (B).

Long Beach Results

At the high tide well, the shallowest sample (2m depth) was consistently fresh in comparison to the deeper samples. This point varied in salinity from 1.2 – 17.8, was steadily high in DO, and represented the transition zone between the thin freshwater lens and the more saline groundwater at depth. From 3 – 5m depth, salinity was relatively constant, ranging from 25.1 – 27.7. Within this depth range, there was a significant decrease in DO and ORP, with all samples exhibiting hypoxic (DO < 3 mg L^{-1}) conditions. While DO content varied from month to month, the consistent hypoxic nature of these samples suggest that geochemical gradients are facilitated by diagenetic and biotic processes. The deepest pore water sample (6m depth), was consistently brackish with salinities varying from 18.4 – 21.4. This deep, high tide well may have sampled a deeper, regional groundwater flow or may have extracted water from a distinctly separate, local geologic unit. DO and ORP of the deepest sample was similar to that of samples from 3 – 5m depth. Low tide and intertidal well salinities varied between 27.0 – 29.9 and 23.8 – 30.2, respectively, with little deviation from month to month. DO content of the low tide and intertidal wells were consistently low at depth and increased towards the sediment-water interface, likely due to oxic seawater infiltration during flood high tide.

Pore water ^{222}Rn distribution beneath Long Beach was much less consistent over the sampling period. Within the high tide well, ^{222}Rn activities varied between 2860 – 4400 Bq m^{-3} for the shallow, brackish sample and from 280 - 3000 for the deeper saline samples. For August, September, and October, there was a local maximum in ^{222}Rn activity of varying magnitude at 3m depth in the intertidal wells. ^{222}Rn activity was highly variable between the low tide and high tide wells (**Figure 1B**).

Discussion

The local maxima of ^{222}Rn and ^{224}Ra at 3m depth beneath Long Beach coincide with a sharp decrease in DO at this depth. The transition from an oxic to hypoxic environment likely reduced sediment bound Mn(hydr)oxides to dissolved Mn^{2+}, resulting in a "pulse" of adsorbed radium and radon released into solution. Within a typical subterranean estuary, such as Callahan's Beach, mixing between fresh groundwater and recirculated seawater often establishes a linear relationship between salinity and radionuclide activity. Knowledge of the fluid composition of interest facilitates the selection of an appropriate groundwater endmember for calculating SGD in radionuclide mass balances (Dulaiova et al. 2008). When fresh SGD is expected to be negligible, the selection of a proper saline endmember becomes more challenging. For example, during August at Long Beach, pore water ^{222}Rn varied from 776-2271 Bq m^{-3} over a salinity gradient between 24.40 and 29.64. These results suggest that ^{222}Rn groundwater endmembers should be sampled closest to the point of pore fluid discharge, in addition to sampling the endmember across salinity gradients (**Figure 2**).

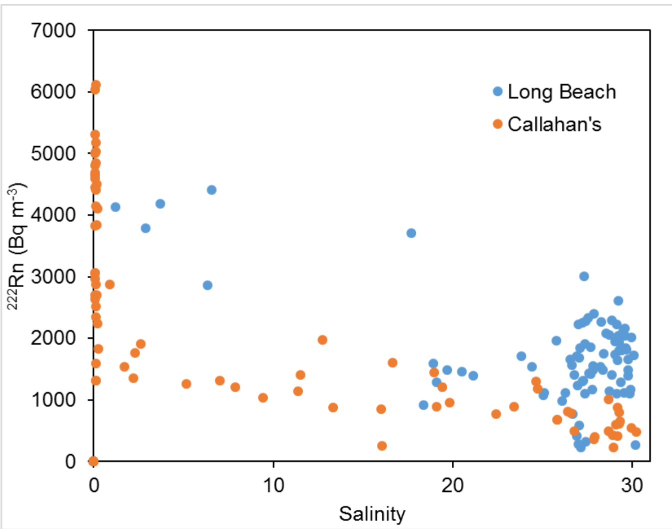

Figure 2. ^{222}Rn variation with pore water salinity, from July – December 2014. Differences between the two field sites suggest that ^{222}Rn is representing two distinct endmembers.

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