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Submarine groundwater discharge driven nitrogen fluxes to Long Island Sound, NY: Terrestrial vs. marine sources

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Abstract

Bottom-waters in Smithtown Bay (Long Island Sound, NY) are subject to hypoxic conditions every summer despite limited nutrient inputs from waste-water and riverine sources, while modeling estimates of groundwater inputs are thought to be insignificant. Terrestrial and marine fluxes of submarine groundwater discharge (SGD) were quantified to Smithtown Bay using mass balances of ^{222}Rn, ^{224}Ra, ^{226}Ra and ^{228}Ra during the spring and summer of 2014/2015, in order to track this seasonal transition period. Intertidal pore waters from a coastal bluff (terrestrial SGD) and from a barrier beach (marine SGD) displayed substantial differences in N concentrations and sources, traced using a multi-isotope approach (^{222}Rn, Ra, δ^{15}N-NO_3^-, δ^{18}O-NO_3^-). NO_3^- in terrestrial SGD did not display any seasonality and was derived from residential septic systems and fertilizer. Marine SGD N concentrations varied month-to-month because of mixing between oxic seawater and hypoxic saline pore waters; N concentrations were greatest during the summer, when NO_3^- was derived from the remineralization of organic matter. Short-lived ^{222}Rn and ^{224}Ra SGD fluxes were used to determine remineralized N loads along tidal recirculation flow paths, while long-lived ^{228}Ra was used to trace inputs of anthropogenic N in terrestrial SGD. ^{228}Ra-derived terrestrial N load estimates were between 20 and 55% lower than ^{224}Ra-derived estimates (excluding spring 2014); ^{228}Ra may be a more appropriate tracer of terrestrial SGD N loads. Terrestrial SGD NO_3^- (derived from ^{228}Ra) to Smithtown Bay varied from (1.40–12.8) * 10^6 mol N y^{-1}, with comparable marine SGD NO_3^- fluxes of (1.70–6.79) * 10^6 mol N y^{-1} derived from ^{222}Rn and ^{224}Ra. Remineralized N loads were greater during the summer compared with spring, and these may be an important driver toward the onset of seasonal hypoxic conditions in Smithtown Bay and western Long Island Sound. Seawater recirculation through the coastal aquifer can rival the N load from terrestrial SGD from a heavily polluted aquifer.

Keywords: Radium isotopes; Radon; Submarine groundwater discharge; Nitrogen; Long Island Sound

1. INTRODUCTION

Coastal eutrophication from excess nitrate (NO_3^-) loading has led to the degradation of numerous coastal ecosystems and has become an environmental issue of global concern (Howarth, 2008). NO_3^- inputs to the coastal ocean may occur through atmospheric N deposition, N_2 fixation, surface water runoff, riverine input, storm-water and waste-water effluent, and submarine groundwater discharge (SGD). SGD is generally composed of a mixture between terrestrial (i.e. fresh), meteoric groundwater discharge driven by a positive terrestrial hydraulic gradient and a marine (i.e. saline) discharge component caused by multiple physical forcing mechanisms, including tidal pumping, wave setup, seasonal-oscillations of the water table and density dispersion along the Ghyben-Herzberg interface

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(Michael et al., 2005; Robinson et al., 2006; Santos et al., 2012). SGD-driven NO_3^- fluxes often rival riverine fluxes, due to the elevated concentration of anthropogenic N in terrestrial groundwater over surface waters (Slomp and Van Cappellen, 2004; Beck et al., 2007b; Knee and Paytan, 2011), which may spatially reflect overlying land-use patterns (Knee et al., 2010; Bishop et al., 2015; Wong et al., 2015; Young et al., 2015). Stable isotopes of nitrogen and oxygen in NO_3^- (δ^{15}N-NO_3^- and δ^{18}O-NO_3^-) has been used successfully as tracers for determining the source of NO_3^- in groundwater (Kendall, 1998; Kendall et al., 2007) and may also reveal the extent of N attenuation mechanisms occurring in SGD (Kroeger and Charette, 2008).

The subterranean estuary (STE) is a biogeochemically reactive zone where groundwater and seawater mix through the coastal aquifer (Moore, 1999). The STE can actively modify the speciation and transport of N to the coastal ocean (Talbot et al., 2003; Slomp and Van Cappellen, 2004; Kroeger and Charette, 2008; Loveless and Oldham, 2010; Weinstein et al., 2011; Erler et al., 2014). Dissolved oxygen gradients and variable pore water residence times in sandy coastal sediments may consume NO_3^- *via* denitrifying bacteria, nitrify NH_4^+ into NO_3^- or remineralize organic matter into inorganic N (Gonneea and Charette, 2014; Goodridge and Melack, 2014). Thus, inland concentrations of N sampled from groundwater monitoring wells may not accurately represent the N endmember in SGD, and excludes any non-conservative N enrichment (or removal) along marine SGD flow paths (Beck et al., 2007b). Marine SGD can act as a significant source of recycled N to the coastal ocean in sandy environments when a physical process, such as tidal pumping, supplies organic matter to the permeable coastal sediment (Charbonnier et al., 2013; Reckhardt et al., 2015; Anschutz et al., 2016).

Marine SGD flow paths occur over various time-scales, ranging from hours or days (tidally driven recirculated seawater; Tamborski et al., 2017) to months or years (due to density dispersion, seasonal oscillations of the water table; Michael et al., 2005, 2011). Radium isotopes (^{223}Ra, ^{224}Ra, ^{226}Ra and ^{228}Ra) can distinguish between short time-scale recirculation processes, including pore water exchange, and those of longer time-scale SGD flow paths (Hong et al., 2017; Rodellas et al., 2017). Naturally occurring ^{222}Rn and radium isotopes have been widely used to estimate the volumetric flux of SGD, as these tracers can spatially integrate SGD signals over large areas (Swarzenski, 2007; Charette et al., 2008). These radionuclides are elevated in pore water relative to surface waters due to alpha recoil following production from the decay of their particle-associated U/Th series parent nuclides. The power of ^{222}Rn and Ra isotopes lies in the range of half-lives of the isotopes; short-lived ^{222}Rn ($t_{1/2} = 3.83$ d), ^{223}Ra ($t_{1/2} = 11.4$ d) and ^{224}Ra ($t_{1/2} = 3.66$ d) can be used to trace tidal processes, while the longer-lived ^{226}Ra ($t_{1/2} = 1600$ y) and ^{228}Ra ($t_{1/2} = 5.75$ y) track seasonal or longer processes and flow paths, as there will be negligible ingrowth of long-lived ^{226}Ra and ^{228}Ra in pore waters driven by short time-scale tidal forcing and pore water exchange processes.

N loading *via* SGD has been shown to fuel harmful algal blooms (Lee et al., 2010) and influence coastal ecology (Miller and Ullman, 2004; Rocha et al., 2015). To consider remedial options, it is important to distinguish between recycled N fluxes to "new" inputs from terrestrial groundwater, because terrestrial flow paths have the potential to be remediated. Here, we use a combined radio (^{222}Rn, ^{224,228}Ra) and stable (δ^{15}N-NO_3^-, δ^{18}O-NO_3^-) isotope approach to quantify SGD and constrain terrestrial and marine nutrient endmembers. We will demonstrate that ^{222}Rn and Ra isotopes can be used to distinguish between terrestrial and marine SGD-driven N loads in sandy, tidal environments. Long-lived ^{228}Ra is applied here to trace terrestrial (freshwater) SGD-driven N fluxes while short-lived radionuclides (^{222}Rn, ^{224}Ra) are used to trace recycled N by organic matter remineralization *via* tidal pumping and wave-setup. We apply this methodology to Long Island Sound (CT-NY, USA) and its smaller embayment, Smithtown Bay, where the mean tidal range is ~2.1 m and the coastline is dominated by sandy beaches (Poppe et al., 2000). Conclusions of our radionuclide mass balances will be independently verified, in part, using manual seepage meters. Both terrestrial and marine SGD flow paths are enriched in N and act as a potentially significant driver for the development of coastal hypoxic events during the summer. By a convergence of these lines of evidence, we intend to show that marine SGD plays a substantial role in conveying N loads on a regional scale.

2. MATERIALS AND METHODS

2.1. Study site

Long Island Sound (LIS) is a coastal estuary adjacent to New York City (USA), lying between the southern shore of Connecticut and the northern shore of Long Island, NY. LIS, including its embayment Smithtown Bay (Fig. 1), has been listed as an estuarine system of national significance by the USEPA's National Estuary Program, in accordance with the Clean Water Act. In western LIS, summertime bottom-water hypoxia has been linked to excessive N inputs from point-source waste-water treatment and industrial facilities (Anderson and Taylor, 2001), as well as the development of water column stratification, which is primarily dependent upon wind-induced current shear (Lee and Lwiza, 2008; Wilson et al., 2008). Previous studies have disregarded groundwater inputs of N to Smithtown Bay, where persistent summertime bottom-water hypoxia was thought to be a function of both the timing and duration of thermal water column stratification and the strength of a counter-clockwise gyre that retains organic matter in the center of the bay (Swanson et al., 2015). For the entire LIS estuary, the ^{224}Ra mass balance-derived total SGD flux is (3.2–7.4) * 10^{10} m^3 y^{-1} (Garcia-Orellana et al., 2014), and is thought to be primarily of a marine origin, driven by tidal pumping (Bokuniewicz et al., 2015). However, previous SGD studies in this region have failed to distinguish terrestrial from marine SGD fluxes, and have not assessed nutrient fluxes from SGD.