Radioactive and Stable Isotope Measurements Reveal Saline Submarine Groundwater Discharge in a Semiarid Estuary

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Abstract

There is little information on submarine groundwater discharge (SGD) in hypersaline estuaries in semi-arid climates where SGD may be the dominant nutrient source. Here, we assess the spatial and temporal variability of SGD in the hypersaline Baffin Bay (Texas) using radon [^{222}Rn], radium [^{226}Ra, ^{224}Ra, and ^{223}Ra], and water isotopes [δ^{18}O and δD]. Continuous electrical resistivity surveys revealed potential SGD at nearshore serpulid reefs. High spatial and temporal resolution radon measurements revealed slightly higher SGD inputs at the shoreline near course-grained sediments and relic serpulid reefs. Mass balance models of ^{222}Rn and ^{226}Ra produced equal SGD estimates within the range of uncertainty, while ^{223}Ra yielded substantially higher SGD rates. Baywide SGD rates from ^{226}Ra, ^{223}Ra, and ^{222}Rn ranged from 1.6±0.2 to 41.3±4.1. Larger SGD rates obtained from short-lived isotopes imply higher recirculated/saline SGD rates over short time scales. Radiogenic and stable isotopes as well as resistivity indicate that saline rather than freshwater accounts for most SGD in this hypersaline estuary. Because saline porewater exchange can play a significant role in coastal biogeochemical budgets, SGD inputs should be considered in management strategies in semi-arid areas where surface inflows are almost absent.

1. Introduction

SGD includes any and all flow of water on continental margins from the seabed to coastal waters (Moore, 2010), including terrestrial (fresh) groundwater and recirculated seawater (Santos et al., 2012a). In estuaries, terrestrial SGD occurs mainly as diffuse seepage from shallow unconfined aquifers along the shoreline and often diffuse over large areas (Knee and Paytan, 2011). A combination of climatologic, hydrogeologic, and oceanographic processes drive SGD. For example, terrestrial hydraulic gradients influenced by short and long term climatic conditions, also respond to physical oceanographic processes such as wave set-up, tidal pumping, and density-driven recirculation, thus affecting rates of SGD (Santos et al., 2012b). While fresh SGD may be equivalent to 4.5±3.2% of global river water fluxes into the oceans (Abbott et al., 2019), recirculated or saline SGD likely exceeds global river volumetric inputs (Cho et al., 2018; Moore et al., 2008). Both fresh and saline SGD can deliver significant amounts of pollutants or dissolved compounds to coastal seas (Su et al., 2014). Indeed, SGD-derived N inputs were greater or similar in magnitude to riverine inputs in a number of local (Rodellas et al., 2018; Wang et al., 2018) and ocean basin scale (Chen et al., 2019; Rodellas et al., 2015a) investigations. However, SGD rates are site specific and can vary by orders of magnitude spatially and temporally.

There is limited information related to the extent of SGD and the role it plays in semiarid regions with minor surface runoff and large evaporation. In these regions, wetlands and estuaries experience hypersalinity (Jolly et al., 2008) often enhanced by anthropogenic impacts (i.e., reduced freshwater inflows due to stream impairments) (Conley et al., 2009; Folk and Siedlecka, 1974; Jolly et al., 2008). Subsurface inflows in dry areas may be comparatively more important due to relatively low surface inflows and atmospheric deposition (Uddameri et al., 2014).

Physical processes such as tidal pumping, wave action, seasonal forcing, convective flow, among other, may drive saline SGD (i.e., seawater recirculation in coastal sediments) and represent a diffuse source of solutes stored in sediments to the surface. Convective flow during the upstream propagation of high salinity waters may cause density inversions at the sediment-water interface, driving episodic saline SGD (Santos et al., 2012b). Dense bioturbator communities may also drive porewater-surface water exchange in some environments (Sandwell et al., 2009; Volkenborn et al., 2007).

Various methods tend to capture different driving forces and scales of SGD. Seepage meters, for example, characterize discharge at specific locations (i.e., m scale) (Charette et al., 2001). Resistivity (Bighash and Murgulet, 2015) and numerical modeling (Uchiyama et al., 2000) require calibration and often quantify fresh SGD. Intercomparison studies at a range of hydrogeologic settings show both discrepancies and agreement among methods (Burnett et al., 2006; Knee and Paytan, 2011). As a result, a combination of methods often builds confidence in estimates and can provide insight into the major components of SGD (i.e., fresh and saline). Isotopic tracers often integrate SGD pathways on time scales comparable to the isotope half-life (Charette et al., 2008; Moore, 1999) at the ecosystem scale (Peterson et al., 2008), but cannot resolve specific SGD mechanisms. When combined with physical methods (e.g., geophysical), tracers allow for improved SGD insight (Peterson et al., 2008).

Radium is often particle-bound in freshwater but is released from particles in contact with brackish water, which makes radium isotopes tracers of brackish or saline SGD (Burnett and Dulaiova, 2003; Charette et al., 2001; Moore, 2006; Peterson et al., 2008). The wide range of radium half-lives ($t_{½}$: ^{224}Ra=3.6 d, ^{223}Ra=11.4 d, ^{228}Ra=5.7 years, and ^{226}Ra=1600 years) allows tracing of SGD over multiple temporal scales (Charette et al., 2001; Peterson et al., 2008). The short-lived isotopes ^{223}Ra and ^{224}Ra are continually regenerated from decay of their thorium parents bound to particle surfaces. In contrast, the long-lived isotopes ^{226}Ra and ^{228}Ra take longer to regenerate (Moore, 2006). Radium isotopes can also reveal residence times in estuaries (Knee et al., 2011) and refine SGD estimates derived from continuous ^{222}Rn concentrations (Burnett and Dulaiova, 2003; Moore, 2006). Radon is much more enriched in both fresh and saline groundwater than surface waters (typically 10-1000-fold or greater) (Burnett and Dulaiova, 2003). Because of its unreactive nature and short half-life ($t_{1/2}$ = 3.83 d), ^{222}Rn can be used to map areas of enhanced SGD (Stieglitz et al., 2010). Continuous, automated time series radon measurements provide high-resolution data (Burnett and Dulaiova, 2003; Burnett et al., 2001) and may allow a reduction in uncertainties when estimating SGD (Sadat-Noori et al., 2015).

Other tracers such as the stable isotopes of oxygen (δ^{18}O) and hydrogen (δD) in water can trace local, regional, and global hydrologic pathways, particularly in groundwater studies (Ide et al., 2020; Li et al., 2019). Only recently the δ^{18}O and δD isotopes have been used in combination with radiogenic isotopes to identify SGD and characterize flowpaths (Rocha et al., 2016; Spalt et al., 2018a). The relationship between δ^{18}O and δD is a valuable tool to understand evaporation and mixing of freshwater and seawater (Bighash and Murgulet, 2015), particularly when coupled with salinity measurements (Rohling, 2013).

Here, we hypothesize that SGD is particularly significant in dry, hypersaline conditions where other solute sources are weak. We quantified porewater flushing rates and SGD during dry and semiwet conditions in a hypersaline, inverse estuary in Texas experiencing recurrent harmful algal blooms (Buskey et al., 2001). Radon and radium isotopes were applied to evaluate total SGD inputs (fresh + saline), while resistivity and stable isotope observations provide insight into preferential flow paths and SGD types (i.e., fresh versus saline). Our results have implications for understanding solute inputs in understudied arid systems that cover long shorelines in the Mediterranean, Africa, Australia and North America.

2. Methods

2.1 Study Area

This study focused on the shallow, well-mixed Baffin Bay in the semiarid Texas coastal plain (**Fig. 1A,B**) in the Gulf of Mexico (Dalrymple, 1964; Simms et al., 2010). There are ongoing concerns that Baffin Bay's ecological health is threatened by persistent brown tides (Wetz et al., 2017). The bay often behaves as an inverse estuary (i.e., higher salinities upstream) due to low freshwater inflows, high evaporation, and limited mixing with the Gulf of Mexico. Los Olmos Creek (**Fig. 1B, Fig. 2**), discharges on average 0.004 $m^3 \cdot s^{-1}$ (min: 0.0 $m^3 \cdot s^{-1}$, max: 1.33 $m^3 \cdot s^{-1}$) (USGS, 2017b), while San Fernando Creek discharges an average of 0.02 $m^3 \cdot s^{-1}$ (min: 0.00 $m^3 \cdot s^{-1}$, max: 0.34 $m^3 \cdot s^{-1}$) (USGS, 2017a). During drought conditions these major tributaries have zero flow. San Fernando Creek receives discharge from 12 wastewater facilities and likely flows permanently downstream of the USGS gauge (Wetz et al., 2017). For this reason modeled freshwater inflows from the Texas Water Development Board (TWDB) were also used in this study which account for precipitation, evapotranspiration, runoff, diversions, and return flows (TWDB, 2019b).

The semiarid area of south Texas is characterized by high evaporation rates that exceed precipitation (60-80 $cm \cdot yr^{-1}$) by about 60 cm annually (Behrens, 1966). The long Bay residence times, often exceeding 1 year, drive extreme salinities as high as 85 during droughts (practical salinity scale; the averaged ocean salinity of 35 is used as the reference (Millero, 1993)). Average salinities are often between 40-50 and may reduce to 1.4 following rare precipitation events (Behrens, 1966; Folk and Siedlecka, 1974; Simms et al., 2010; Wetz et al., 2017). These conditions make this bay a schizohaline environment changing from fresh to hypersaline conditions (Folk and Siedlecka, 1974). The effects that hypersalinity has on SGD are poorly understood in Baffin Bay and elsewhere (Jolly et al., 2008).

The coastal plain catchment gradient is gentle at approximately 0.8 $m\cdot km^{-1}$ (Simms et al., 2010), leading to low surface runoff and high infiltration into sandy soils. The shoreline in the upper reaches of Baffin Bay consists of bluffs 2 to 4 m high that grade down to tidal flats. The bay is isolated from the Gulf of Mexico by Padre Island and is further insulated from the contiguous Laguna Madre System by shallow reefs (Simms et al., 2010). The nearest inlets that allow exchange between Baffin Bay and the Gulf of Mexico are Packery Channel and Aransas Pass (~41 km and ~70 km north of Baffin Bay, respectively) and Port Mansfield (~80 km south) (Wetz et al., 2017). Strong southeast winds of 16 to 32 $km\cdot h^{-1}$ are dominant from February to August (Dalrymple, 1964; Rusnak, 1960). From September to February, the dominant wind direction shifts northwest with an average speed of 18 $km\cdot h^{-1}$ (Lohse, 1955; TCOON, 2016). Baffin Bay (**Fig. 1C**) has an average depth of 2 m (max: 3 m) (Simms et al., 2010) and experiences small astronomical tides (<0.1 m) (Simms et al., 2010). With the strong, persistent winds, the water depth is mainly controlled by wind (Breuer, 1957; Militello, 1998) making the estuary well-mixed with little vertical stratification.

Baffin Bay is generally in direct contact with the Chicot aquifer at many locations (Anaya et al., 2016), the shallowest regional hydrostratigraphic unit. Chicot, along with the Evangeline, and Jasper aquifers, are part of the major Gulf Coast Aquifer (GCA), with a sand thickness ranging from 200 m in the south to 400 m in the north, and an average freshwater saturated thickness of about 300 m (George et al., 2011). Average horizontal hydraulic conductivities of the Chicot aquifer within 121 km of the coast are 14.2 $m\cdot d^{-1}$ (range: 9.8 $m\cdot d^{-1}$ to 19.2 $m\cdot d^{-1}$) and the highest ($\bar{x}$: 18.6 m·d^{-1}) occur within 80 km of the coast (Young et al., 2016). GCA is a leaky artesian aquifer system comprised of a complex of clays, silts, sands, and gravels (Ashworth and Hopkins, 1995; Waterstone and Parsons, 2003) overlaid by eolian plain and barrier island deposits and alluvium (Shafer and Baker, 1973). The southern area including Baffin Bay, is almost completely covered by a sand sheet with a maximum thickness of >18 m. Surface drainage is almost absent with much of the precipitation infiltrating into the sandy aquifer (Shafer and Baker, 1973).

The upper 15 m of bay bottom sediments consist of multiple layers of clayey-silt, muds, and muddy sand facies, with finer sediments in the center of the bay. Sandy spits and serpulid reefs have been found throughout the bay (Simms et al., 2010). A sandier "Upper Bay" facies is present along the shorelines with intrusions scattered throughout the bay center (Simms et al., 2010). Groundwater in the unconfined aquifer flows toward the coast, eventually discharging into the bays and estuaries (Breier et al., 2010; Mace et al., 2006; USDA, 2012; Waterstone and Parsons, 2003). Average annual base flow of groundwater from the GCA to surface water (e.g. streams, creeks, and the ocean) is approximately 0.46 m^3·s^{-1} to 0.47 m^3·s^{-1} in Kleberg and Kenedy Counties, respectively (Anaya et al., 2016). Deep groundwater input is not expected to occur in this bay due to lower than sea level hydraulic heads (TWDB, 2019a). In the deep aquifers, drawdowns exceeding 46 m may occur in the Kingsville area, near Baffin Bay (Chowdhury et al., 2004). Changes in water levels in this formation were insignificant from 1933 to 1969. These changes ranged from a decline of 0.3 m to a rise of 0.5 m, with most water levels above sea level (Shafer and Baker, 1973), thus groundwater input from the deeper aquifers is not expected.

Brackish groundwater (total dissolved solids of 1,000 mg·L^{-1} or more) is common in the southern GCA (George et al., 2011). While the salinity of groundwater in the aquifer increases naturally in deep parts, the southern coastal part of the aquifer contains significantly higher chloride, sulfate, and sodium than the onshore northern part (Mace et al., 2006). Shafer and Baker (1973) indicating that shallower units are not a suitable water supply.

2.2 Electrical Resistivity Profiling

Observations commenced with mobile, continuous electrical resistivity profiling (CRP) to gain insight into the underlying shallow stratigraphy and locate potential zones of SGD (Cross et al., 2014; Murgulet et al., 2016). In brief, we used an Advanced Geosciences, Inc. SuperStingR8 Marine system with a 112 m cable consisting of 56 graphite electrodes and induced polarization imaging system. The depth of penetration for this system is ~22 m with a resolution of 50% of the electrode spacing (i.e., 2 m spacing and 1 m spatial resolution) (Advanced Geosciences, 2017). Three CRPs were collected in January 2016 (**Fig. 1D**). Interpretation of inverted images resulted in the selection of eight radium sampling locations along the CRP transects and four time series radon monitoring stations (**Fig. 1C**).

2.3 Water Sample Collection and Measurements of Radium Isotopes

2.3.1 Sample collection

Surface water samples were collected at eight stations during spatial and time series sampling events in January, July and November 2016, to characterize SGD inputs under different environmental conditions. Field parameters (i.e., temperature, dissolved oxygen (DO), pH and salinity) were measured using a YSI multiparameter sonde. To characterize regional aquifers, groundwater samples were collected from six USGS wells screened at depths between 187-383 m. Before sample collection, the wells were purged of three volumes or until field parameters stabilized. Shallow porewater samples were also collected at multiple locations within the bay using a push-point piezometer (AMS Retract-a-Tip) inserted 0.7 to 3.2 m below the sediment-water interface (i.e., deep enough to prevent contamination of porewater with surface water) (Charette and Allen, 2006). Before collection, the tubing was flushed until the sample was clear and field parameters stabilized.

2.3.2 Radium and Radon measurements

For radium measurements, between 45 to 60 L of surface water was collected from ~0.2 m above the sediment-water interface. Radium processing was conducted using established techniques (Kim et al., 2001). Measurements for ^{223}Ra and ^{224}Ra analysis were conducted on a Radium Delayed Coincidence Counter (RaDeCC) within three days of collection (Moore, 2006). Processing of Mn fibers for ^{226}Ra followed methods described by Kim et al. (2001) while measurements were conducted using a RAD-7 (Peterson et al. (2008). Extraction efficiencies of Mn fibers were determined to be 99% for ^{223}Ra, 98% for ^{224}Ra and 96% for ^{226}Ra by processing random samples through a second Mn cartridge. The counting uncertainty were ≤10% for ^{224}Ra and ^{223}Ra and ≤8% for ^{226}Ra.

Measurements of ^{222}Rn in surface water were conducted both at stationary (i.e., time series at stations 9 through 12, see **Fig. 1C**) and mobile continuous (along the same transects as the CRP, **Fig. 1D**) modes in July and November 2016. Time series sampling at station 12 in July was performed within 24 hours of a 51 mm precipitation event. Measurements of ^{222}Rn for the endmember porewater and groundwater were done using a Durridge RAD7 radon-in-air monitor with a soda bottle and the WAT250 protocol (Lee and Kim, 2006). For stationary/time series and mobile/spatial measurements, we measured ^{222}Rn from a constant stream of water passing through an air-water exchanger (Dulaiova et al., 2005). Water from ~0.2 m below the air-water interface was pumped via a peristaltic pump to the RAD AQUA air-water exchanger. Air was then pumped from the exchanger to three Durridge RAD-7 radon-in-air detectors connected in sequence. The method requires a minimum of 30 minutes for radon to reach equilibrium in the water-air exchanger (Dulaiova et al., 2005). Our 30 min integration time ensures a more accurate reading in the low concentration environment investigated. Three RAD7's were used in series to increase the frequency of the readings and provide the desired spatial resolution (i.e., a ^{222}Rn measurement every 10 minutes or one measurement every ~660±10 m). Coordinates and depth were recorded simultaneously with a Lowrance LMS-480M sonar GPS and an LGC-2000 GPS Antenna.

2.3.4 Stable Isotopes

Measurements of δ^{18}O and δD in groundwater, pore-and surface- water were conducted to evaluate the contribution of fresh versus saline SGD. Deuterium excess (d-excess = $\delta D - 8 \times \delta^{18}O$, Dansgaard (1964)) was determined to evaluate the effect of evaporation for each season and sampled environment. Samples were filtered through 0.7 µm GF/F in the field and analyzed using a Picarro L2120-I cavity ringdown spectrometer at the Texas A&M University, Stable Isotope Geoscience Facility. The isotope ratios were referenced to the international Vienna Standard Mean Oceanic Water (VSMOW) using internal reference standards (JGULF: 1.22 ‰ δ^{18}O and 5.8 ‰ δD and KONA: -6.86 ‰ δ^{18}O and -50.8 ‰ δD) and are reported using the delta (δ) notation in per mil (‰). Average internal precision was ±0.12‰ for δ^{18}O and ±0.36 ‰ for δD, and external precision (i.e., an internal standard with multiple aliquots measured throughout an analytical session) was ±0.26 ‰ for δ^{18}O and ±1.1 ‰ for δD.

3.3 Submarine Groundwater Discharge Estimates

Rates of total SGD were calculated using the ^{223}Ra, ^{226}Ra, and time series ^{222}Rn mass-balances. Radium mass-balance provides an evaluation of baywide scale SGD, while time series ^{222}Rn measurements give insight into more localized SGD. Given the likely heterogeneity of the groundwater inputs and the expected spatial and temporal variability of degassing due to wind effects, mobile ^{222}Rn measurements were used as a qualitative indicator of SGD in this study. Time series ^{222}Rn measurements were performed over 6 to 12 hours, depending on location and weather conditions (e.g., winds >5 m s^{-1} make sampling unsafe due to waves).

3.3.1 Radium-derived SGD rates

Radium-based SGD estimates were determined using apparent water ages, surface runoff, and the porewater and groundwater measurements as the source endmembers. Porewater was selected as an endmember given that its geochemical characteristics reflect mixing of terrestrial and marine (i.e., recirculated seawater) sources. Any deep groundwater short-lived radium isotope would approach equilibrium with near surface sediments before entering surface water (Knee et al., 2011). For comparison purposes, SGD rates were also determined using the ^{226}Ra activities of the deep groundwater endmember. Activities of ^{223}Ra were not measured in groundwater. The minimum, average and maximum radium activities of the available samples was used to estimate the potential range in SGD rates. A mixing model following Moore (2006) was use to relate the fairly conservative $\delta^{18}O$ and long-lived ^{226}Ra to identify the porewater endmember for radium mass balance calculations. First, the two variables were displayed in a cross-plot graph to assess mixing between surface water and porewater samples. The apparent relative contributions of porewater endmembers to surface water signatures were used to select the porewater endmembers for the two seasons.

The radium apparent age of the surface water, or the relative time (T_r) since the radium first entered the system, is an essential term used to calculate SGD rates (Swarzenski et al., 2007), calculated using the ratio of the short-lived ^{224}Ra to the longer-lived ^{223}Ra or ^{226}Ra isotopes (Dulaiova and Burnett, 2008; Knee et al., 2011; Moore, 2000):

$$T_r = \frac{AR_{GW} - AR_{CO}}{AR_{CO} \times \lambda_{224}} \tag{1}$$

where AR_{GW} is the initial activity ratio of discharging groundwater, AR_{CO} is the measured activity ratio (AR) at the station of interest, and λ_{224} is the decay constant (d^{-1}) for the short-lived ^{224}Ra isotope. This equation assumes radium activities and ARs are higher in the radium source than in the receiving nearshore surface water. Consequently, ARs should be decreasing as the water mass is moving away from the source due to radioactive decay and mixing.

Desorption experiments using sediment cores at the time series locations showed that the sustained flux of dissolved ^{226}Ra from bottom sediments generates a small inventory (0.02 $Bq \cdot m^{-2}$) that is negligible for this system (see section 4.3.1). Therefore, we assume that the major source of ^{226}Ra is SGD and ignore sediment diffusion or resuspension in the mass balance (see eq. 2). Similarly, sediment supported ^{223}Ra inventories were found to be negligible (3.1×10^{-6} $Bq \cdot m^{-2}$), thus they were ignored in the mass balance. Because of the long half-life of ^{226}Ra ($t_{½}$ = 1,600 yr), its decay rate may be neglected. However, ^{223}Ra decay was accounted for.

To estimate SGD from ^{226}Ra or ^{223}Ra observations in Baffin Bay, a mass balance was developed. This includes all sources of radium other than groundwater, including tidal exchange, riverine input, desorption from riverine suspended sediments, and diffusion from bay bottom sediments (Moore, 1996). Excess ^{226}Ra ($^{226}Ra_{ex}$ [$Bq \cdot d^{-1}$]), or ^{223}Ra ($^{223}Ra_{ex}$ [$Bq \cdot d^{-1}$]) fluxes in the bay equal:

$$^{226;\,223}Ra_{ex} = \left[\frac{(^{226;\,223}Ra_{BB} - {}^{226;\,223}Ra_{sea})V_{bay}}{T_r}\right] - \left[^{226;\,223}Ra_r Q_r\right] - \left[^{226;\,223}Ra_{des} Q_r\right] + \left[^{223}Ra_{BB}(1 - e^{\lambda_{223} T_r})V_{bay}\right] \qquad (2)$$

where $^{226\text{ or }223}Ra_{BB}$ is the average measured ^{226}Ra, or ^{223}Ra, activity in Baffin Bay; $^{226\text{ or }223}Ra_{sea}$ is the average ^{226}Ra, or ^{223}Ra, activity in the offshore water body (i.e., Laguna Madre), which exchanges tidally with Baffin Bay; V_{bay} is the volume of Baffin Bay; T_r is the residence time estimated from equation 1; Q_r is the average discharge of the tributaries to the bay; $^{226\text{ or }223}R_r$ is the average ^{226}Ra, or ^{223}Ra, activity of the tributaries; $^{226\ \mathrm{or}\ 223}Ra_{des}$ is the activity of ^{226}Ra, or ^{223}Ra, desorbed by the sediments in the bay (Swarzenski, 2007); and λ_{223} is the decay rate of ^{223}Ra as is shown in the final term of the equation where the decay of ^{223}Ra is corrected. The last term in the equation is only applied for ^{223}Ra, as the half-life of ^{226}Ra is so long (1,600 years) that decay is negligible. After accounting for all the sources of ^{226}Ra, or ^{223}Ra, it is assumed that the excess fluxes from equation (2) is the result of SGD. Using a porewater endmember activity ($^{226\ \mathrm{or}\ 223}Ra_{PW}$), SGD is calculated from:

$$SGD_{^{226;\,223}Ra} = \frac{^{226;\,223}Ra_{ex}}{^{226;\,223}Ra_{PW}} \qquad (3)$$

To determine the radium input from riverine discharge, we performed radium desorption experiments using riverbed sediment samples (i.e., 0 -10 cm) from the freshwater portion of each creek. Los Olmos Creek had a consistently high salinity (>60), which should cause desorption of any sediment bound radium and was not considered a source for suspended sediment-bound radium (Webster et al., 1995). Low salinity creek water (San Fernando: 2.63 and Petronila: 9.85) samples and high salinity bay water (55) were filtered through Whatman GF/F filters to remove suspended solids and processed through MnO_2 fibers to reach radium-free status. Different salinity solutions of radium-free creek and bay water were prepared to match bay salinities at the time of sample collection (January: 32, July: 37, November: 51). A known mass of dried sediments was added to a known volume of the Ra-free solutions, in proportions mimicking total suspended solids (TSS) in the study area (40-100 mg·L^{-1}, with 100 mg·L^{-1} used for all events to produce a conservative estimate of SGD) (Ward and Armstrong, 1997). Sample solutions were stirred for one hour before passing through MnO_2 fibers to extract the desorbed radium (Gonneea et al., 2008).

To determine contribution of ^{226}Ra, or ^{223}Ra, from the tributary creeks into the bay, the total activity was normalized to the sediment mass and then multiplied by the annual sediment flux from the creeks using freshwater inflow (TWDB, 2019b). The model includes not just ephemeral creek discharges, but surface runoff from all the watersheds feeding into the bay and return flows to the creeks.

3.3.2 Radon mass balance

Stationary time series measurements of ^{222}Rn were used to construct a mass balance and inventory as described in detail by Burnett and Dulaiova (2003); Lambert and Burnett (2003); Smith and Robbins (2012), and references therein. Activities of ^{222}Rn in water from the mobile measurements matched closely, or were lower than, the activity of ^{226}Ra in surface water on some occasions. This resulted in negative $^{222}Rn_{ex}$ inventories, preventing the development of a complete ^{222}Rn mass balance for estimating SGD. Instead, to qualitatively evaluate the spatial or temporal SGD inputs, excess ^{222}Rn inventories (I) were calculated:

$$I = [z(A_{Rn} - A_{Ra})] \quad (4)$$

where A_{Rn} is the activity of ^{222}Rn in the water column, A_{Ra} is the dissolved ^{226}Ra in the water column, z is depth. Except for one event with wind speeds >5m s^{-1}, most time series ^{222}Rn measurements exceed ^{226}Ra allowing the construction of a ^{222}Rn mass balance using the above-mentioned references.

With the microtidal characteristics of this system, tidal effects are expected to be minimal compared to wind-driven circulation (Santos et al., 2012a). Changes in water levels of <0.3 m are recorded in Baffin Bay due to tides throughout the day (NOAA, 2014). Therefore, tidal effects were not addressed here but water levels are accounted for in the radon inventory calculations. It was assumed that the lower radon inventories were due to mixing with offshore waters with lower radon activity. To further constrain SGD inputs, the maximum absolute values of the observed negative fluxes during each time series after corrections for atmospheric emissions (Burnett and Dulaiova, 2003) were used to correct radon fluxes for losses via mixing. Sediment-supported radon activities were measured using laboratory sediment equilibration experiments with cores ranging from 21 cm to 62 cm deep collected at each time series station (Corbett et al., 1998). Activities of ^{226}Ra in surface waters at high and low tides during the stationary monitoring and each spatial sampling location were used to correct for in-situ production of ^{222}Rn.

4. Results and Discussion

4.1 Continuous Resistivity Profiling

The inverted CRPs (**Fig. 1D**) along with local geology maps revealed likely locations of SGD. Resistivity ranged from 0.18-1.1 Ω-m (**Fig. 3**), indicating sediments saturated with high salinity water (Murgulet et al., 2016). Subsurface saline-freshwater interfaces may exist under bays (Cross et al., 2014), but we found no evidence of fresh-surface water mixing in our study. The typical average resistivity for freshwater saturated sediments such as clay or sandy loam are 38 Ω-m and 51 Ω-m, respectively (Nyquist et al., 2008). In this study, the hypersaline nature of porewaters (**Fig. 4),** and the presence of coarse to black mud sediments (Dalrymple, 1964) (**Fig. 1D**) explain the relatively narrow and small electrical resistivity values. Eight locations with higher electrical resistivity (0.45-0.90 Ω-m, stations 1 through 8 in **Fig. 1C**) near potential connections between the subsurface and surface water (**Fig. 3**) were deemed areas of interest (Nyquist et al., 2008) for additional assessments.

Areas of higher resistivity such as F and G on the northern transect (**Figs. 1D and 3**) coincided with occurrences of serpulid reefs (Dalrymple, 1964). Serpulid reefs grow on sandy substrates (Simms et al., 2010), potentially providing a preferential groundwater flow path (Spalt et al., 2018a). Larger SGD may also occur in areas with slightly higher resistivity, aligned with the more coarse-grained sediments along the coastlines (**Fig. 1D**). These locations coincide with the sandier "Upper Bay" facies (Simms et al. 2010) extending along the shoreline and sporadically intruding the center of the bay. These areas appear in the CRP images as higher resistivity features at the sediment -water interface. Areas of interest such as E and C coincided with some of these intrusions near the bay bottom (**Fig. 3**). Lower resistivities in the central bay are indicative of low permeability sediments dominated by anoxic black muds (Simms et al., 2010). The black mud, with a maximum water content of 78% (Dalrymple, 1964) of saline to hypersaline nature, lead resistivities lower than those of dry clay (Nyquist et al., 2008) as seen in the southern transect. There was no evidence of fresh SGD under any paleo-valley interfluves in Baffin Bay. The salt- fresh- water interface is likely much further inland or much deeper than was measured in this study (Krantz et al., 2004; Sawyer et al., 2014a).

4.2 Radium Observations and Mass Balance

Porewater activities of ^{224}Ra, ^{223}Ra and ^{226}Ra were greater in July ($\bar{x}$: 72.3±7.2, 2.5±0.3, and 43.6±4.4 Bq·m^{-3}, respectively) and are associated with an increase in salinity (**Fig. 4, Table 1**). As opposed to surface water that showed minor negative correlations between salinity and radium, in porewater activities increased with salinities, in particular ^{226}Ra. These differences in porewater activities indicate either change in inputs, and/or in redox conditions. Average groundwater radium activities (^{226}Ra: 46.5±4.7 Bq·m^{-3} and ^{224}Ra: 50.0±5.0 Bq·m^{-3}, respectively) (**Table 2**) were comparable to shallow porewaters, though samples were collected from >187 m deep bores. The ^{226}Ra range observed in this study was consistent with those observed in shallow, brackish groundwater by Breier and Edmonds (2007) (1.4– 11.7 Bq·m^{-3}), Douglas et al. (2020) (3.8-16.2 Bq·m^{-3}) and similar to the average ($\bar{x}$: 12.1 Bq·m^{-3}) found by Spalt et al. (2018a) in other Texas coastal sites. Giving these similarities among the shallower units, and no observed salinity dependence, we estimated SGD rates using the shallowest and the average groundwater radium (i.e., ^{224}Ra and ^{226}Ra) signature.

The highest ^{226}Ra in surface water was measured during the warm and low precipitation season in July ($\bar{x}$: 18.4 Bq·m^{-3}; n=8), and the lowest in the colder and slightly wetter season in January ($\bar{x}$: 14.0 Bq·m^{-3}; n=8) and November ($\bar{x}$: 15.7 Bq·m^{-3}; n=10) (**Fig. 4, Table 1).** The highest activities occurred at stations 6 and 3 near a serpulid reef with higher electrical resistivity, while the lowest activities were consistently measured towards Laguna Madre. The greater July surface water activities are accompanied by greater porewater activities **(Table 2)**.

The overall average ^{224}Ra activity was 14.9±1.5 Bq·m^{-3} (n=24). The highest mean activity for all events was 21.7 Bq·m^{-3} at station 1 in Laguna Salada while the lowest of 11.5 Bq·m^{-3} was measured at station 3 (**Fig. 4, Table 1**). Like ^{226}Ra, the highest overall ^{224}Ra activity was in July (24.7±2.5 Bq·m^{-3}) (**Fig. 4**). The overall average ^{223}Ra activity was 0.85±0.1 Bq·m^{-3} (n=16) across all seasons. The highest ^{223}Ra activity recorded was 2.2±0.2 Bq·m^{-3} in July at station 5 while the lowest occurred at stations 2 and 7 (0.3±0.03 Bq·m^{-3}).

Based on the most accurate ^{226}Ra and δ^{18}O mixing model results (Figure 5), the representative input to the bay (i.e., endmembers) in July is assumed to be the mean of all porewater excluding the outlier station 8. In November porewater from stations 3 and 1 were identified as the most likely sources. Thus, radium SGD calculations used the mean porewater (except for station 8) in July, and the mean of stations 1 and 3 in November. An important consideration in the selection of endmembers was the distance to surface waters, location in the bay, and the dominant wind and current direction. Another consideration for the endmember selection was their robustness, evaluated by inspecting the salinity and $\delta^{18}O$ mixing model (not shown) as well as ^{226}Ra enrichment of porewater.

Residence time changes the ratio of long to short lived isotopes of source waters. Deeper groundwater has high activities of longer-lived isotopes compared to porewater and recirculated water in which short-lived isotopes are more enriched, reflecting in calculated radium ages (Duque et al., 2019).With the average $^{224}Ra/^{226}Ra$ ARs of groundwater identified as the endmember, the estimated radium ages were the lowest in July followed by January (**Fig. 6A, B**). In November, the groundwater endmember led to much longer ages reflecting distant groundwater inputs or a different signature. With the porewater AR, radium ages are in closer seasonal agreement. Using the porewater endmember, radium ages were longer in November. A slight discrepancy in July occurred at the Petronilla Creek inlet (station 5; **Fig. 6B**) where radium ages were negative when compared to 0 days using the groundwater endmember. For both endmembers, the radium age is negative (i.e., -3.9 days) at the Laguna Madre mouth, implying that these assumptions (i.e., pair $^{224}Ra/^{226}Ra$ and the porewater and groundwater endmember signatures) fail to capture small scale changes. Negative ages are explained by disproportionally more input of the short-lived isotope in relation to the long-lived in surface water (Dulaiova and Burnett, 2008; Knee et al., 2011; Moore, 2000). Station 8 is affected by inputs from sources external to the bay, due primarily to constant wind-driven surface flow from Laguna Madre. Station 5 is located close to the mouth of Petronella Creek which flows year-round due to upstream discharges. In both instances, mixing of water with different signatures is expected to cause dilution of local SGD.

Using the seasonal changes in radium signatures in porewater and surface water, ^{226}Ra based SGD rates were higher in July (6.4 ± 0.6 cm·d^{-1}) than November (1.6 ± 0.2 cm·d^{-1}). In comparison, the average groundwater radium endmember yields SGD rates of similar magnitudes (January: 4.6±0.5 cm d^{-1}; July: 5.8±0.6 cm d^{-1}; November: 1.2±0.1 cm d^{-1}). Groundwater signatures are assumed constant across seasons, thus, the increase in radium activities in surface water in July translates to larger SGD rates. Lower surface water activities in November, and January, result in lower SGD because the groundwater activity exceeded porewater activity. Thus, there is a clear indication that time-constrained porewater activities are the preferred endmember in SGD estimates.

Ages derived using the porewater ^{224}Ra/^{223}Ra ARs were similar in July and November (**Fig. 6E and F**) to those determined from ^{224}Ra/^{226}Ra ARs. The resulting baywide SGD rates had similar trend to ^{226}Ra estimates (**Table 3, Fig. 7**), but were larger in magnitude both in July (41.3±4.1 cm·d^{-1}) and November (33.6±3.4 cm·d^{-1}). This difference in magnitude could be attributed to the release of ^{223}Ra during wind-driven sediment resuspension. Enhanced inputs of short-lived isotopes was observed following resuspension due to ship traffic in Spain (Rodellas et al. (2015b). In sediments continuously flushed by saline water, the shorter lived isotopes (e.g., ^{224}Ra, and ^{223}Ra) regenerate faster (Rodellas et al., 2015b), leading to greater inputs than the long-lived isotopes (e.g., ^{226}Ra) (Moore, 2006).

4.3 Radon Observations and Mass Balance

Shallow porewater ^{222}Rn activities were much lower than deep groundwater (**Tables 2 and 3**), implying dilution and decay along flow paths, or exchange with low concentration surface waters driven by seawater recirculation. Deep groundwater ^{222}Rn activities are comparable to the shallow aquifers north to Baffin Bay, in the Aransas and Nueces watersheds, ranging between 5,660 and 14,500 Bq·m^{-3} (Murgulet et al., 2018; Spalt et al., 2018b). Given the low porewater activities and to prevent overestimating SGD rates, the groundwater radon signature was used as the groundwater endmember to model ^{222}Rn-derived SGD (see section 4.3.1).

Mobile measurements of surface water ^{222}Rn over 30-minute integration steps resulted in relatively large standard deviations ($\bar{x}$: 9.96 Bq/m^3). This variability is not supported by ^{226}Ra activities that were consistent across the bay (**Table 4**). Thus, other factors such as wind, mixing, and heterogeneity in SGD fluxes explain changes in the spatial distribution of radon. The spatial variation in ^{222}Rn activity had a significant inverse relationship with wind speed (R^2: 0.4; p-value: $\ll$0.001, n=139) (**Fig. 8A**). Slow winds often occur early in the day and peak in the afternoon (**Fig. 2**), degassing ^{222}Rn from the water column (Wanninkhof, 1992). However, the large variability in ^{222}Rn inventories for wind speeds > 2 m/s argues for two populations of data with no significant correlation of wind speed and negative ^{222}Rn inventory at higher wind speeds. Given that different areas were surveyed on different days, spatially variable SGD could also be argued, with wind speed as the cause for the negative inventories. This implies that ^{222}Rn in groundwater is more spatially variable than indicated by the deep well samples or the literature values. These effects were observed in both seasons as a significant number of surface water ^{222}Rn activities were below those supported by ^{226}Ra decay and lead to multiple instances of negative inventories (**Fig. 8, 9**). Many of these low activities were recorded during high wind speeds but also along the muddy bottoms from Laguna Madre mouth to Laguna Salada.

Shallow water and pervasive antecedent wind-driven waves and white capping in Baffin Bay prevent an accurate accounting of radon atmospheric evasion. To partially account for loss due to degassing, radon activities were adjusted by adding back the equivalent of the lowest observed surface water ^{226}Ra activity as an estimate of the expected background ^{222}Rn. This correction reduces the number of negative inventories (**Fig. 8**) and further demonstrates the significant effects of degassing and the need for high spatial resolution measurements.

Mobile measurements of radon across the bay reveal larger inventories at locations along the northern shoreline (**Fig. 9**). As also implied from CRP imagery, these nearshore radon hotspots match locations of remnants serpulid reefs (Dalrymple (1964) (**Fig. 1**). Sites 6 and 3 overlie, or lie close to, serpulid reefs located on sandy substrates (Simms et al., 2010) that are excellent conduits of SGD and preferential flow paths (Sawyer et al., 2014b) (**Figs. 1 and 3**). Higher than average radon inventories ($\bar{x}$ for July: 4.1±22.5 Bq·m^{-2} and November 12.3±33.9 Bq·m^{-2}) were measured for both stations 6 (July: 6.6±23.3 Bq·m^{-2} and November: 21.9±18.5 Bq·m^{-2}) and 3 (July: 14.9±10.1 Bq·m^{-2} and November: 23.8±12.8 Bq·m^{-2}, respectively). The ^{226}Ra and δ^{18}O mixing models (**Fig. 5**) also identify stations 6 surface water and station 3 porewater as major contributors of surface water signatures.

Enhanced exchange at serpulid reefs is expected to be accompanied by more unique porewater chemistry when compared to stagnant environments. Porewater at station 3 (extracted from 1 to 1.8 m depths) had surface water-like salinities and more depleted stable isotope signatures, consistent with effective exchange. All other porewaters maintained a salinity 10 units greater than surface water, implying lower freshwater inputs or exchange. This provides further evidence that serpulid reef structures enhance SGD through preferential exchange paths. SGD may provide favorable environmental conditions to oyster reefs due to preferential inputs of freshwater and nutrients associated with small-scale heterogeneity (i.e., paleovalley environments; Spalt et al., 2019; Spalt et al., 2018). Indeed, coral reefs can benefit from submerged springs (Cantarero et al., 2019; Moosdorf et al., 2015). The potential for terrestrial inputs in proximity to reefs has ecologic and economic implications since SGD nutrient fluxes can be important on a local scale (Luijendijk et al., 2020). This is an especially important aspect to consider in management decisions in low gradient, semiarid watersheds in areas with sporadic surface inflow.

4.3.1 Time series radon mass balance to estimate SGD rates

When the porewater radon activities are used to model SGD, the resulting rates are orders of magnitude higher that those previously reported for this area or for other semiarid environments. For instance, seepage meters measured SGD rates up to 48 $cm \cdot d^{-1}$ near this study's site 3 and 9 (Uddameri et al. (2014). With the groundwater activities as the preferred radon endmember, and comparison to previously reported rates, we assessed possible uncertainties in SGD estimates as related to the available activity ranges: (1) the lowest groundwater ^{222}Rn activity (2,040 $Bq \cdot m^{-3}$); (2) the average of the six available groundwater sample activities ($\overline{x}$ = 7,805 $Bq \cdot m^{-3}$) and (3) the highest groundwater ^{222}Rn activity (15,376 $Bq \cdot m^{-3}$).

The lowest groundwater ^{222}Rn activities yield SGD rates that are unrealistically high (see **Table 4**) when considering the local conditions. Given the semiarid climate with low precipitation rates and reduced aquifer recharge, these estimates are the most unrealistic. On the other hand, the average and highest groundwater ^{222}Rn endmembers result in reasonable SGD rates, comparable to previous studies in this study area and in similar climates (Douglas et al., 2020; Spalt et al., 2018a). The highest ^{222}Rn activity groundwater endmember results in conservative SGD estimates at about half those determined using the average groundwater. These results also align with the short-lived radium mass balance estimates and are close to seepage meters from Uddameri et al. (2014). The SGD rates derived using the maximum radon groundwater activities are thus assumed to be the most realistic in July (range: 5-14 $cm \cdot d^{-1}$; $\overline{x}$: 10.6 $cm \cdot d^{-1}$) and November (range: 8-27 $cm \cdot d^{-1}$; $\overline{x}$: 13 $cm \cdot d^{-1}$).

4.4 Stable Isotopes of Oxygen and Hydrogen

Surface water $\delta^{18}O$ and δD abundances were enriched across all three seasons ($\delta^{18}O$ $\bar{x}$: 2.14‰ ± 0.1‰ and δD $\bar{x}$: 13.3‰ ± 1‰; $\bar{x}$ d-excess: -4.1‰; n=23; see **Figs. 9 and 10A**). All signatures fell below the global meteoric water line (GMWL) and the Waco meteoric water line (WMWL) but are above the line formed by local groundwater (**Fig. 10**). Values of $\delta^{18}O$ and δD were lower in January ($\delta^{18}O$ $\bar{x}$: 0.8‰ and δD $\bar{x}$: 7.2‰; n=7) than July ($\delta^{18}O$ $\bar{x}$: 3.0‰, and δD $\bar{x}$: 17.2‰; n=8) and November ($\delta^{18}O$ $\bar{x}$: 3.0‰ and δD $\bar{x}$: 18.3‰; n=8) (**Fig. 11A**). This enrichment above marine signatures implies evaporation (Gat and Tzur, 1967; Walther and Nims, 2015) as a result of persistent winds and increasingly warmer temperatures (Katz et al., 1997) from winter to summer and fall.

Recent investigations revealed more depleted isotope signatures in estuaries to the north of Baffin Bay (i.e., Mission-Aransas and Nueces estuaries) ($\delta^{18}O$ range: -2.5‰ to 2.1‰ and δD range: -7.22 to 13.9‰) but, overall, with similar seasonal trends (Murgulet et al., 2018; Murgulet et al., 2015). During the major rain events in warm months, significant freshwater inputs decrease stable isotope values as also noticed in estuaries in Australia and Florida (Price et al., 2012).

The increasing effects of evaporation from the colder to warmer and dryer seasons are supported by the transition from positive to negative d-excess (January, July, and November $\bar{x}$ d-excess: 1.1‰, -7.0‰; and -5.8‰; **Fig. 11B**), although a correlation with salinity was not found. The $\delta^{18}O$ of precipitation and humidity is the dominant signal recorded in the January surface water when evaporative effects were minimum. This is beyond expected inputs of isotopically lighter precipitation (Craig, 1961) brought by air masses from the northwest in late fall and winter (Lohse, 1955; TCOON, 2016). The lack of correlation between the isotopic values with salinity is evidence of consistent seawater recirculation in sediments homogenizing and buffering seasonal changes in the signatures of surface- and pore- water.

Seasonality drives the isotope characteristics of precipitation due to cyclic changes in ocean temperature and air-sea interactions (Gat, 1996). This affects δD of receiving reservoirs (**Fig. 11B**). From spring to late fall, isotopically heavier rain events are expected to dominate as the marine Gulf air masses move inland. Isotopic mixing and dilution of individual rainfall events with surface water affected by evaporation and minimum freshwater inflows lead to a progressive shift toward more enriched signatures during warm months (**Fig. 11A**). Nevertheless, the isotope signature in January also approaches that of marine sources even though the prevalent wind direction and the minimal water exchange with the Gulf of Mexico imply negligible input of Gulf waters.

Although salinities were higher in porewater, the $\delta^{18}O$ and δD abundances were more depleted ($\delta^{18}O$ $\bar{x}$: 1.6‰ and δD $\bar{x}$: 10.1‰; $\bar{x}$ d-excess: -2.7‰; n=17) than surface water. Similar to surface water, the lowest abundances in porewater ($\delta^{18}O$ $\bar{x}$: 1.3‰ and δD $\bar{x}$: 9.7; $\bar{x}$: d-excess: -0.8‰; n=5) were measured in January. However, the overall increase in isotopic values is not as significant from the cold to warm months, explained by lagged mixing effects between surface and porewater. While depleted terrestrial signatures may be contributing, these isotopic values imply no significant inputs of freshwater to porewaters. Because these samples plot along a porewater - surface water mixing line, they further support our interpretation of saline SGD in the upper meter of sediments.

Source changes within porewater may result in signature differences between surface water and porewater as the ambient porewater mixes with more depleted terrestrial or seawater inputs. If mixing with isotopically depleted and fresher waters occur, decreases in salinity are also expected, which was not observed in this study (**Fig. 11**). Surface water-porewater mixing would also alter the porewater signature to reflect evaporative effects as indicated by the d-excess (**Fig. 11B**), although this process is also associated with an increase in salinity. Water-clay interaction may also slightly enrich ^{18}O and δD , but the increase in salinity is expected to be four-fold (Gat, 1996), which was also not observed here. Alternatively, salinity may increase when anhydrous evaporite deposits dissolve, without significantly changing the isotope composition of the fluid. There is evidence of hydrous evaporites in the sediments (Bighash and Murgulet, 2015; Simms et al., 2010), therefore it is likely that some anhydrous evaporites like halite are present as well.

5. Implications of SGD to Semiarid and Hypersaline Estuaries

Radium ages estimated in this study are dependent on radium activities of both porewater and surface water, which may have been affected by changes in the porewater chemistry (e.g., salinity, ORP, pH) (Kadko et al., 1987) rather than SGD inputs. Radium desorption is predicted to reach a maximum at a salinity of approximately 20 (Elsinger and Moore, 1980; Webster et al., 1995). Thus, because salinities in a semiarid and hypersaline estuary are well above seawater, no effects on radium activities are expected. There are many processes that may influence the activities of dissolved radium within a hypersaline, semiarid estuary, creating challenges to identify the endmembers contributing to SGD. Heterogeneities in the geologic and geochemical makeup of the local subsurface can cause significant spatial and temporal variability in the radon and radium content of the pore fluids and the upland groundwater (Duque et al., 2019; Krantz et al., 2004; Sawyer et al., 2014a).

In the increasing hypersaline conditions during dry and hot conditions, microorganisms create anoxic environments that reduce sediment-bound metal oxides, releasing radium into porewater (Tamborski et al., 2017). During warm conditions when primary production is higher, organic matter decomposition could enhance radium desorption and porewater activities (Kadko et al., 1987). Radium may be scavenged during the biogenic precipitation of minerals (Bishop, 1988; Krest et al., 1999) and/or desorbed from sediments under hypoxic conditions due to remineralization. This is expected to result in larger inputs of ^{224}Ra and ^{223}Ra and lower inputs of ^{226}Ra, as observed in this study. Thus, if production occurs in the porewater between seasons, constant rates of SGD will increase radium in surface water (see section 3.3.1). In the absence of seasonal porewater characterization, higher radium activities could be perceived as larger SGD. Although, the short lived ^{223}Ra resulted in higher SGD rates than ^{226}Ra, there was no large difference between the two warm and colder seasons. Short-lived isotopes could lead to larger SGD rates due to sediment disturbances caused by increased ship traffic or faster regeneration times (Rodellas et al. (2015b). Strong, persistent winds over Baffin Bay may also contribute to the sediment release of short-lived isotopes to the water collumn.

While radium may only provide the saline portion of SGD (Moore, 2006), the ^{222}Rn provides insights into total SGD (fresh + saline groundwater) (Burnett and Dulaiova, 2003). The selection of a representative groundwater endmember for estimation of SGD fluxes is challenging (Burnett and Dulaiova, 2003; Cerdà-Domènech et al., 2017; Garcia-Orellana et al., 2013a; Garcia-Orellana et al., 2013b; Lamontagne et al., 2008; Urquidi-Gaume et al., 2016a, b) and can result in large uncertainties. When using radon, uncertainty of SGD estimates derived from selection of the groundwater endmember were significant, and likely larger than those derived from mass balance error propagation (Urquidi-Gaume et al. (2016a). Characterization of porewater for use as the groundwater endmember results in lower uncertainties, as shown here with radium-derived SGD rates. However, porewater ^{222}Rn is often deficient in shallow sediments (Cable and Martin, 2008).

These difficulties prevent us from quantifying possible freshwater inputs. In hypersaline and semiarid environments, sporadic land-derived/fresher SGD inputs are expected following rain events (Rocha et al., 2016). However, this contribution is small when compared to the saline inputs (i.e., recirculated, or saline groundwater inputs), which dominates SGD to the estuary year-round as supported by lack of evidence of freshening in the subterranean estuary (**Fig. 4A'**). Because of the persistent hypersaline nature of porewater and shallow groundwater, and the significant degassing of radon, radium is the preferred groundwater tracer in semiarid, hypersaline, wind-dominated systems. The selection of the most appropriate SGD quantification approach in those systems requires consideration of several factors such as tracer enrichment in the groundwater/porewater relative to surface water, the ability to quantify the sources and sinks of the tracers, and most importantly, tracer reactivity in the environment.

6. Conclusion

We assessed SGD in a hypersaline, shallow estuary in a semiarid climate using a combination of techniques. Continuous resistivity surveys revealed the heterogeneous nature of sediments, including reef areas along the northern shore that seem to be significant SGD hotspots. The spatial ^{222}Rn survey supported resistivity observations. Radium measurements revealed seasonal variability in SGD estimates. ^{223}Ra-derived SGD rates exceed those from ^{226}Ra likely due to the faster regeneration of the short-lived isotopes allowing the quantification of faster seawater recirculation processes. In hypersaline, and often hypoxic estuaries, with no significant inputs of terrestrial freshwater, salinity has indirect effects on the water radium activities within porewaters. The choice of a tracer endmember has significant implications on the SGD estimates as it can lead to large uncertainties as discussed in other studies. Radium was likely the most reliable groundwater tracer given the dominant saline inputs, and the challenges in constraining a radon mass balance in a windy, shallow system. The large saline SGD rates likely release significant fluxes of nutrients, carbon, and trace metal into the coastal ocean.

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