THE IMPACT OF SUBMARINE GROUNDWATER DISCHARGE ON NUTRIENT DYNAMICS IN A SUB-POLAR MUDFLAT

By
Josianne Haag, B.Sc.

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of

Master of Science in
Oceanography

University of Alaska Fairbanks
August 2022

APPROVED:
Amanda Kelley, Committee Co-Chair
Ana Aguilar-Islas, Committee Co-Chair
LeeAnn Munk, Committee Member
Mark Johnson, Committee Member
Russell Hopcroft, Chair
Department of Oceanography
Bradley Moran, Dean
College of Fisheries and Oceans Science
Richard Collins, Director of the Graduate School
Abstract

Submarine groundwater discharge (SGD) plays a major role in the hydrological and biogeochemical cycles controlling nearshore nutrient availability. The Northern Gulf of Alaska coastline is highly diverse, ranging from rocky beaches, sandy beaches, and mudflats; SGD varies according to sediment permeability, strength of wave pumping, and slope of the water table. SGD has been previously estimated at a rocky beach in the NGA, but this thesis sought to quantity SGD in an extensive mudflat using well-established tracers (radium and radon) and determine the major sources of nutrients to the bay. The rate of SGD was comparable between the mudflat and rocky beach (233 ± 245 and 260 ± 360 cm day⁻¹, respectively), and both locations were significant sources of nitrate and silicic acid, and sinks of phosphate. Offshore water also provides a major input of nitrate and phosphate to the bay. Thus, there is no single dominant source for all macronutrients, consequently, multiple processes must be considered when predicting nutrient cycling.
# Table of Contents

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
</tr>
<tr>
<td>List of Figures</td>
</tr>
<tr>
<td>List of Tables</td>
</tr>
<tr>
<td>Acknowledgments</td>
</tr>
<tr>
<td>Chapter 1 General Introduction</td>
</tr>
<tr>
<td>1.1 Groundwater as a Source of Nutrients</td>
</tr>
<tr>
<td>1.2 Water Residence Time as a Control on Biogenic Processes</td>
</tr>
<tr>
<td>1.3 A High Latitude Estuary with Extensive Mudflats: Jakolof Bay, Alaska</td>
</tr>
<tr>
<td>1.4 Naturally Occurring Radioisotope Tracers</td>
</tr>
<tr>
<td>1.5 Outline</td>
</tr>
<tr>
<td>1.6 References</td>
</tr>
<tr>
<td>Chapter 2 Methodology</td>
</tr>
<tr>
<td>2.1 Description of Model Site</td>
</tr>
<tr>
<td>2.2 Estimating Flux of Submarine Groundwater Discharge (SGD)</td>
</tr>
<tr>
<td>2.3 Partitioning Between Freshwater and Recirculated Seawater in SGD</td>
</tr>
<tr>
<td>2.4 References</td>
</tr>
<tr>
<td>Chapter 3 The Role of Submarine Groundwater Discharge to the Input of Macronutrients within a Macrotidal Subpolar Estuary</td>
</tr>
<tr>
<td>3.1 Abstract</td>
</tr>
<tr>
<td>Section</td>
</tr>
<tr>
<td>----------------------------------------------</td>
</tr>
<tr>
<td>3.2 Introduction</td>
</tr>
<tr>
<td>3.3 Methods and Materials</td>
</tr>
<tr>
<td>3.4 Results and Discussion</td>
</tr>
<tr>
<td>3.5 Conclusions</td>
</tr>
<tr>
<td>3.6 References</td>
</tr>
<tr>
<td>Chapter 4 General Conclusion</td>
</tr>
<tr>
<td>4.1 Methodological Improvements and Novel Approaches</td>
</tr>
<tr>
<td>4.2 Major Findings</td>
</tr>
<tr>
<td>4.3 Future Directions</td>
</tr>
<tr>
<td>4.4 References</td>
</tr>
</tbody>
</table>
List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1.1</td>
<td>A schematic diagram demonstrating the fresh and saline layers of groundwater discharge occurring in an aquifer</td>
<td>5</td>
</tr>
<tr>
<td>Figure 2.1</td>
<td>A theoretical mass balance model of water to estimate SGD</td>
<td>18</td>
</tr>
<tr>
<td>Figure 2.2</td>
<td>The portions of the three natural decay chains starting as $^{235}$U, $^{238}$U, and $^{232}$Th that includes the parent and daughter isotopes of Ra and Rn, useful tracers of groundwater</td>
<td>19</td>
</tr>
<tr>
<td>Figure 2.3</td>
<td>Schematic diagram of the RAD-7 system in the continuous sampling layout</td>
<td>21</td>
</tr>
<tr>
<td>Figure 2.4</td>
<td>Schematic diagram of the RAD-7 system in the discrete sampling layout</td>
<td>22</td>
</tr>
<tr>
<td>Figure 2.5</td>
<td>A theoretical mass balance model of $^{222}$Rn to estimate SGD</td>
<td>24</td>
</tr>
<tr>
<td>Figure 3.1</td>
<td>Map of the study area sampled during three seasons at neap tide: autumn 2020, spring 2021 and summer 2021</td>
<td>64</td>
</tr>
<tr>
<td>Figure 3.2</td>
<td>An experiment using glacial river water and increasing its salinity with NaCl indicates a linear relationship with the desorption of $^{224}$Ra until a salinity of 15</td>
<td>74</td>
</tr>
<tr>
<td>Figure 3.3</td>
<td>The variation in salinity of the GW passing through the temporary PVC wells deployed in the upper mudflat of Jakolof Bay</td>
<td>75</td>
</tr>
<tr>
<td>Figure 3.4</td>
<td>A theoretical diagram depicting the saltwater interface moving landward during the incoming tide and moving seaward during the outgoing tide</td>
<td>76</td>
</tr>
<tr>
<td>Figure 3.5</td>
<td>Variation in total excess $^{222}$Rn (Bq m$^{-3}$) in the ambient seawater with tidal change</td>
<td>77</td>
</tr>
<tr>
<td>Figure 3.6</td>
<td>The $^{222}$Rn surveys conducted at high tide and low tide in Jakolof Bay</td>
<td>80</td>
</tr>
<tr>
<td>Figure 3.7</td>
<td>The water column in Jakolof Bay over a tidal cycle</td>
<td>86</td>
</tr>
<tr>
<td>Figure 3.8</td>
<td>There is a significant relationship ($p &lt; 0.05$) with the natural log of $^{224}$Ra and distance from the head of the bay</td>
<td>89</td>
</tr>
</tbody>
</table>
**Figure 3.9** The N:P in Seldovia Bay decreases from winter to late summer in 2019, before increasing in autumn.

**Figure 3.10** The relationship between N:P and distance from the head of the bay.

**Figure 4.1** Tidal amplitude across the Northern Gulf of Alaska.
List of Tables

Table 1.1 Methods to estimate submarine groundwater discharge ........................................ 9

Table 2.1 The extraction efficiencies of Ra from seawater under varying flow rates (L min⁻¹) and Ra activities (dpm 100 L⁻¹) ........................................................................................................ 33

Table 2.2 The ideal progeny of radium isotopes with energy peaks that can be detected above background on a gamma spectrum ........................................................................................................ 43

Table 2.3 University of Alaska Fairbanks RaDeCC performance results for ²²⁴Ra and ²²³Ra analysis performed on all four counters ........................................................................................................ 46

Table 3.1 The total and fresh SGD estimates using independent measurements across various tidal stages and seasons ........................................................................................................ 79

Table 3.2 Nutrient inputs to Jakolof Bay in spring and summer 2021 ........................................ 88

Table 3.3 The concentration of nutrients in the river, GW, surface seawater, and depth-integrated offshore waters across seasons in Jakolof Bay ................................................................. 90
Acknowledgments

This thesis was written at the University of Alaska Troth Yeddha’ campus on the unceded traditional homelands of the Lower Tanana Dené. This research was conducted as a guest working on the unceded traditional homelands of the Dena’ina and Alutiiq peoples.

I am grateful to Dr. Amanda Kelley, Dr. Ana Aguilar-Islas, Dr. Henrietta Dulai, Dr. William Burt, Dr. Mark Johnson, Dr. LeeAnn Munk, Emily Ortega, Marina Alcantar, Shelby Bacus, James Currie, Jonah Jossart, and Feyne Elmore for their aid during fieldwork, lab work, and the writing of this thesis. Thank you to Dr. Roger Kelly who generously loaned us radium standards which made this project possible. My research was financially supported by the Coastal Marine Institute, Bureau of Ocean Energy Management, and the Alaska Established Program to Stimulate Competitive Research (EPSCoR) program. Thank you to the Northern Gulf of Alaska Long Term Ecological Reserve and the National Oceanic and Atmospheric Administration (NOAA) National Estuarine Research Reserve System for use of their data.
Chapter 1 General Introduction

The coastal ocean represents most of the productive regions in the global ocean due to its tight link to the terrestrial domain. The open ocean, which makes up nearly three-fourths of the Earth, is often considered a biological desert in large part due to nutrient supply limitations. However, the 10% of the ocean that constitutes upwelling zones and coastal waters support much of the world’s fisheries (Ryther, 1969). The Northern Gulf of Alaska (NGA) is supplied with nutrients from (1) the deep ocean during periods of weak upwelling in summer when the along-shore winds relax from the typical downwelling circulation (Royer, 1998), (2) winter mixing that supplies nutrients to support the spring bloom, and (3) the formation of eddies near the coast that entrain nutrient-rich continental water into the surface of the open ocean (Crawford et al., 2007). Along some coasts, hotspots of phytoplankton growth are observed where the river plume mixes with the seawater (Liu and Dagg, 2003) demonstrating how coastal biogeochemistry fuels the coastal marine food web.

A major component of the hydrological cycle and coastal biogeochemistry is groundwater, a field of study that has received increased interest in the last two decades (Moore, 2010). In the Atlantic and Indo-Pacific Oceans, groundwater flux is three to four times greater than the flux of rivers and is considered the dominant pathway for land-derived materials entering the ocean (Kwon et al., 2014). Groundwater has been shown to provide more nutrients to coastal ecosystems than rivers in many local studies, like South Carolina (Crotwell and Moore, 2003; Krest et al., 2000), the South Sea of Korea (Kim et al., 2003), Brazil (Niencheski et al., 2007), the Philippines (Taniguchi et al., 2008), Thailand (Burnett et al., 2007), the Mediterranean (Rodellas et al., 2015), and China (Zhang et al., 2020). The coastline along the NGA is highly diverse, ranging from rocky shorelines to sand beaches to mudflats (Field and
Groundwater flux can vary greatly between these locations due to differences in sediment permeability, strength of wave pumping, and slope of the water table (Santos et al., 2021). The only estimate of groundwater in the NGA is from a rocky beach where its flux was a significant source of NO$_3^-$, silicic acid (SiO$_4^{4-}$), iron, and nickel (Lecher et al., 2016a; 2016b; 2017; Dimova et al., 2015). Two independent methods of measuring groundwater discharge conducted at the same location resulted in a difference in rate of an order of magnitude (Lecher et al., 2016a; Dimova et al., 2015), thus requiring additional estimates of groundwater to further support the hypothesis that groundwater nutrient discharge can rival that of rivers across the entire NGA (Lecher et al., 2016b).

1.1 Groundwater as a Source of Nutrients

Groundwater is a critical component of nutrient flux and biogeochemical cycling in Alaskan waters. The flow of any water – regardless of fluid composition or driving force – from a subterranean estuary into the sea is referred as submarine groundwater discharge (SGD) (Burnett and Dulaivova, 2003). It is comprised of three possible fluid components that mix within a coastal aquifer and undergo chemical reactions with aquifer solids. The three major components of SGD are (Burnett and Dulaivova, 2003):

1. Meteoric water (“fresh SGD”) originating as atmospheric precipitation that percolates into the water table and is driven by a hydraulic gradient.

2. Recirculated seawater (“saline SGD”) driven by oceanic processes such as wave pumping, wave set-up or set-down, and tidal pumping wherein seawater injected into permeable sediments mixes with sediment pore water enriched in dissolved solutes before being drawn back into the ocean.
3. **Connate waters** created as the salinity of groundwater within an aquifer is increased by the dissolution of salts (will not be discussed further as the NGA is not recognized as having substantial evaporites).

While 70 % of global SGD enters the ocean in the Indo-Pacific Oceans (Kwon et al. 2014), there is a critical lack of research in this field in polar and sub-polar regions (Santos et al., 2021). The NGA includes some coastal embayments (e.g., Cook Inlet) that have some of the world’s greatest tides (up to 8 m) that can potentially produce high rates of saline SGD (Larson et al., 2013). This region may also have high rates of fresh SGD due to the steep topography along the coast which creates a strong hydraulic gradient. The SGD reported from the rocky beach in southcentral Alaska ranges from 16 cm day^-1^ to 260 ± 360 cm day^-1^ (n=149) (Lecher et al., 2016a; Dimova et al., 2015) while the average SGD rate in the Pacific Ocean is an order of magnitude lower (2-22 cm day^-1^; Santos et al., 2021).

With continued climate change, the role of SGD as a source of nutrients will become more important. The composition of water from glacier-fed rivers will be altered with continued glacier recession. There will be decreased PO_4^{3-} and NO_3^- rich dissolved organic matter but increased dissolved organic carbon, specific conductivity, and dissolved organic N and dissolved inorganic N (Hood and Berner, 2009). Over time, the relative magnitudes of nutrient discharges in coastal ecosystems may shift to favor other sources, such as groundwater, due to changes in the hydrological cycles over the course of a warming planet.

SGD is typically enriched in nutrients with respect to seawater (Burnett and Dulaiova, 2003). Before flowing into the ocean, SGD spends time in a subterranean estuary, a coastal aquifer in which freshwater from land drainage mixes with percolating seawater (Moore, 1999). The chemical reactions that occur between the mixed water and aquifer solids alter the fluid
The four general reactions that occur include (Moore, 2010):

1. Desorption of ions from aquifer solids due to the increased ionic strength from percolating seawater (see section 1.4 for an example using radium).
2. Remineralisation of organic matter which releases carbon, nutrients, and metals into groundwater.
3. Dissolution and precipitation of carbonates.
4. Oxidation-reduction reactions that produce and consume metal oxides, which can release or sequester other ions.

The chemical reactions that can occur within the aquifer are partially controlled by the origin of the water in the subterranean estuary. Saline SGD, driven by oceanic processes such as wave pumping or tidal pumping is the dominant driver of SGD flux in many areas (Burnett and Dulaiova, 2003; Kim et al., 2003; Taniguchi et al., 2008; Liu et al., 2017). Saline SGD is typically oxygenated, which alters the redox conditions in the aquifer so that trace metals such as iron and manganese precipitate out as oxides. Recirculated seawater can also introduce excess organic ligands which bind to elements such as copper, removing them from the SGD-signal (Lecher et al., 2016b). In southcentral Alaska, our understanding of SGD composition is limited to a single study in a rocky beach (Kasitsna Bay). Here, SGD is composed of primarily recirculated seawater, with only 1% of SGD supported by topographically driven terrestrial fresh groundwater (Dimova et al., 2015). However, fresh SGD can introduce new nutrients instead of supplying the coastal ocean with regenerated nutrients. The flow of fresh and saline SGD is delineated with fresh groundwater flowing above saline groundwater due to differences in density, with a saltwater interface separating the two layers (Fig. 1.1). This pattern is repeated
below a confining layer. Therefore, the predominant chemical reactions can change drastically with depth in an aquifer.

**Figure 1.1** A schematic diagram demonstrating the fresh and saline layers of groundwater discharge occurring in an aquifer. The fresh layer sits above the denser saline layer, a pattern which repeats below a confining layer. The layer between where the fresh and salt fractions mix is the saltwater interface. Adapted from Moore (2010).

The intertidal substrata influence the rate of SGD and the resulting nutrient fluxes to the coastal ocean. The rate of SGD is greater at sandy beaches compared to mudflats or tidal marshes, with the greatest flow occurring in the upper intertidal zone and near rivers (Qu et al., 2017; Santos et al., 2021). The rate of SGD can influence the chemical reactions within an aquifer, as lower SGD translates to longer residence time within an aquifer where oxygen will become depleted, and denitrification will occur (Qu et al., 2017). While SGD tends to be a source of $\text{NO}_3^-$, aquifers are a sink of $\text{PO}_4^{3-}$ (Qu et al., 2017; Lecher et al., 2016b). Due to the large range of intertidal substrata along the NGA coastline, understanding the total flux of SGD across the region requires determining the SGD in various substrate types. A rocky beach has already been investigated by Lecher et al. (2016a; 2016b; 2017) and Dimova et al. (2015), but
there is a paucity of data for sand beaches and mudflats in sub-polar regions. The present study estimated SGD in the NGA in a mudflat to validate the larger extrapolation of the entire coastline made by Lecher et al. (2016b), as well as consider the relative importance of SGD compared to offshore water as a source of nutrients in the NGA.

1.2 Water Residence Time as a Control on Biogenic Processes

Water residence time, i.e. the flushing rate of water, controls the availability of nutrients to primary production. In southcentral Alaska, the limiting factor for total phytoplankton cell abundance and standing biomass are nutrient availability and grazing by predators (Doroff and Holderied, 2018). The longer the residence time (i.e., the slower water is moving through an ecosystem), the more opportunity there is for phytoplankton to assimilate available nutrients. Increased river flow associated with accelerated glacier melt could decrease the residence time of coastal waters and limit the time nutrients are available to primary producers.

Additionally, water residence time in a coastal ecosystem influences chemical and biological processes that are essential for fish and shellfish stocks. These processes include nutrient provisioning for primary production supporting food webs, larval dispersal of economically and ecologically important shellfish (e.g., clams, Tanner crabs), and the distribution of zooplankton communities that function as an essential food source for commercially important fish species (e.g., herring, salmon) (McGowan et al., 2020). Residence time also affects the dispersal of ichthyoplankton and benthic invertebrate larvae that spend days to months as plankton (Murphy and Iken, 2014, McGowan et al., 2020).

Within an estuary, the water residence time can vary over physical and temporal space. A primary mechanism driving water flow over time is tidal forcing. At neap tides when the tidal
range is narrowest, the freshwater fluxes from rivers play a larger role versus spring tides when the range of the tidal prism is larger, and the residence time is shortened (Yuan et al., 2007). Residence time can also be affected at flood tide when tidally driven inflow is subducted under the buoyant outflow from an estuary, creating a transient static intrusion front (Thain et al., 2004). Identifying the controls behind the successional dynamics of community composition in estuaries requires a stronger understanding of the physical conditions present.

Biogenic processes are also indirectly affected by water residence time through the transport and deposition of sediment. The speed of tidal currents is dependent on water depth, meaning a wave crest will propagate faster than a trough. This asymmetry across the tidal cycle increases current velocity during flood tide compared to ebb tide that results in a net transport of suspended sediment uptide near the seafloor (Allen et al., 1980). There is a progression from well-winnowed sands in the main tidal channel to mud-dominated sediments at the high tide level where the current speed drops close to zero and finer material settles out of the water column (Allen et al., 1980). Beyond sediment-specific community composition, the resulting burial of benthic invertebrates from sedimentation can threaten populations based on their motility, vertical position, and the potential for exposure to anoxic conditions during burial (Hinchey et al., 2006). Furthermore, the gradient in permeability of sediment from porous sand to cohesive, non-permeable mud across the seafloor will affect the SGD flux coming from the intertidal and the various constituents discharged concurrently.

1.3 A High Latitude Estuary with Extensive Mudflats: Jakolof Bay, Alaska

As a sub-bay in southcentral Alaska, Jakolof Bay is an ideal site to study SGD flux from a high latitude region with extensive mudflats. First reported in 1915 by the US Geological
Survey, Jakolof Bay’s unique, well-drained soils consist of very deep volcanic ash layered over alluvial deposits. The rock is primarily highly metamorphosed graywacke and slate, with minor amounts of limestone and basic igneous material (Moxham and Nelson, 1950). This bay is conducive to high rates of SGD due to a large tidal range (over 8m), and a steep hydraulic gradient created by high mean annual precipitation (450 to 800mm).

The river discharge in this bay is minimal relative to the glacier-fed rivers nearby. Jakolof River has no glaciation in its watershed which makes river discharge highest in spring when fed from precipitation and melting snowpack, and often dries up in late summer. As the river goes subterranean a few times before entering Jakolof Bay, it is likely that there is a significant contribution of baseflow (pers. comm. Michael Opheim, Jan 10, 2022). The river originates at Red Mountain, which is composed primarily of dunite with some pyroxenite (Guild, 1942). In the early 20th century, the area was mined heavily for chrome, and in the 1960s and 1970s the South-Central Timer Company logged the heavily forested valley. This resulted in a road and gravel airstrip added to the bay which makes this bay more accessible for fieldwork.

To the best of my knowledge, this study represents the first SGD flux to be calculated from a high latitude mudflat, which will allow for a more accurate extrapolation to the role of SGD along the coastline of the NGA when considered with the previous studies in the region (i.e., Lecher et al., 2016a; Dimova et al., 2015). The water residence time of this bay is also vital to the local economy since the bay currently supports an oyster farm. Finally, this is proof of concept that can be applied to countless other bays across Alaska with critical subsistence harvest.
Objective: Quantify the seasonal and tidal variations in the rates of SGD flux and assess its role in driving local nutrient budgets in a sub-bay.

- **Hypothesis 1:** Tidal pumping is the primary mechanism behind driving SGD flux into Jakolof Bay.

- **Hypothesis 2:** SGD is the primary source of nutrients into Jakolof Bay, outweighing riverine inputs and offshore water.

- **Hypothesis 3:** The water residence time within Jakolof Bay is on the same timescale as the tidal sequence.

1.4 Naturally Occurring Radioisotope Tracers

Capturing the fresh and saline SGD fractions requires the use of multiple methods. There are **three general approaches to the assessment of groundwater** (Table 1.1; Burnett and Dulaiova, 2003).

**Table 1.1 Methods to estimate submarine groundwater discharge.**

<table>
<thead>
<tr>
<th>Method</th>
<th>Description</th>
<th>SGD measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modelling</td>
<td>Varies from simple mass balance calculations of onshore groundwater to complex numerical models of subsurface flow</td>
<td>Fresh SGD</td>
</tr>
<tr>
<td>Direct physical measurement</td>
<td>Seepage meters and measurement of the hydraulic gradient</td>
<td>Fresh SGD or total SGD</td>
</tr>
<tr>
<td>Tracer technique</td>
<td>Natural geochemical species or artificial tracers</td>
<td>Total SGD</td>
</tr>
</tbody>
</table>

This thesis is focused on assessing groundwater as a proxy for nutrient flux to the nearshore using natural geochemical tracers. Due to the removal of chemical constituents by biology, an ideal tracer for SGD will behave conservatively in the water column with no
bioactivity or particle reactivity. In southcentral Alaska, NO$_3^-$ and Si(OH)$_4$ levels were low in surface waters but a conservative tracer had an elevated concentration that suggests that SGD flux was high, but the nutrients were removed by biology (Lecher et al., 2016b). An appropriate tracer for estimating SGD flux must include measurable sources and sinks within an ecosystem so that a mass balance approach can be utilized. The nutrients from SGD can be estimated by multiplying the SGD by the concentration of a nutrient in porewater.

Radium (Ra) is an ideal tracer of land-derived hydrological sources. In reducing groundwater, Ra is dissolved in either its free state (Ra$^{2+}$) or complexed with sulfates RaSO$_4^0$ (Langmuir and Riese, 1985). This allows the element to be mobile in subterranean waters. However, its mobility is restricted when adsorbed to iron or manganese hydroxides in oxidizing conditions (Gainon et al., 2007a; Gainon et al., 2007b) or to clays (Riese, 1982), or co-precipitated with barium or strontium (Langmuir and Melchior, 1985). It has been shown that the desorption of Ra from these precipitates increases with salinity to a threshold where full desorption is reached (Sturchio et al., 2001; Webster et al., 1995) and low pH (Almeida et al., 2004). The intrusion of seawater into shallow groundwater will increase the cation exchange between the ions in seawater and the available binding sites on clay particles, allowing more Ra to dissolve into the water (Kwon et al., 2014). In coastal waters, an increase in [Ra] dissolved in the water column indicates a water flux from land.

Radon-222 ($^{222}$Rn) is preferential to Ra as a tracer of SGD. Radon, the daughter isotope of Ra, is a noble gas, and thus will escape any open system by outgassing to the atmosphere. In rivers, which are open to the atmosphere, the only reason for detectable $^{222}$Rn to be present is if there is a supply from baseflow. Therefore, when $^{222}$Rn is detected in marine waters, it is assumed to originate from groundwater (Burnett et al., 2006, Eröss et al., 2012). Ra is diluted in
saline SGD because it is more mobilizing in reducing versus oxidizing conditions (Gainon et al., 2007a) where the intrusion of oxygenated seawater into the permeable sediment during flood tide precipitates iron-oxides (Lecher et al., 2016b) that are highly efficient at adsorbing Ra (Eröss et al., 2012). In addition, Ra has detectable activities in rivers so using this tracer requires constraining an additional source. However, rivers are not a significant source of $^{222}$Rn due to outgassing, but in groundwater $^{222}$Rn can build up in the presence of dissolved or adsorbed Ra. Therefore, $^{222}$Rn will be more concentrated than Ra in SGD entering the coastal environment relative to ambient seawater, making the tracer more distinguishable from background.

Using $^{222}$Rn and Ra isotopes together provides complementary information about the coastal hydrology of biogeochemical systems. The four isotopes of Ra decay at different rates; thus, changes in isotope ratios present in the water column can be used to estimate water residence time (Moore, 2000). $^{222}$Rn, measured using a continuous detector, can be used to characterize SGD via two approaches. First, $^{222}$Rn surveys along a stretch of shore can identify SGD hotspots (Dulaiova et al., 2010). Second, continuous monitoring in one location can detect changes in SGD over timescales such as those induced by tidal pumping (Liu et al., 2017). Furthermore, the ratio of $^{222}$Rn to $^{226}$Ra in porewater has been used to determine the extent to which deep, anoxic aquifers are mixing with shallow, oxygenated aquifers. The short half-life of $^{222}$Rn ensures that $^{222}$Rn in shallow groundwater must have originated there or nearby. $^{226}$Ra can originate from the deeper aquifer, so this ratio can inform the amount of mixing between the two layers, as well as the aquifer’s capacity for cation exchange (Gonneea et al., 2008). Together, the use of Ra and $^{222}$Rn isotopes can provide more information on the extent to which SGD is influencing the coastal environment than either tracer independently.
1.5 Outline

This thesis is written with each chapter as a stand-alone document. Chapter 2 provides a detailed methodology for Ra and \(^{222}\text{Rn}\) sampling and analysis. Chapter 3 tackles the objectives of the thesis. Chapter 4 is a general conclusion discussing the major findings of this research and future directions that can be investigated in this region.
1.6 References


Chapter 2 Methodology

The following section provides a detailed description of the sampling and analytical methods used throughout the present research. The radioactive tracers utilized in this thesis were radon-222 ($^{222}$Rn) and radium (Ra). We extensively reviewed tracer-based approaches—including sampling, analyzing, and data processing—for future studies that aim to use these tracers in a high latitude estuary with a large tidal range.

2.1 Description of Model Site

Jakolof Bay, a small sub-bay located in the larger Kachemak Bay estuary, served as a model site to estimate submarine groundwater discharge (SGD). This is primarily due to specific features that include high rates of groundwater flow resulting from a large tidal range (over 8 m), and a steep hydraulic gradient created by high mean annual precipitation (450 to 800 mm). Unlike most of the rivers in this area, the river at the head of Jakolof Bay is not glacier fed and can dry out completely in summer, relying on groundwater to supply nutrients. The mudflat composes approximately 15% of the 4 km long, shallow bay that reaches a maximum depth of 13 m (average 8 m). This bay contains a high diversity of invertebrate fauna (Lees et al., 1980), and dramatic annual blooms and die-off cycles of dense kelp beds of *Saccharina* (Miller and Kelley, 2021).

To estimate the SGD rate from the mudflats at the head of Jakolof Bay, we modelled the flow of water through Jakolof Bay as a mass balance (Fig. 2.1) where we solved for SGD using the sources and sinks of water. While most of the fluxes can be estimated, saline SGD is difficult
to accurately quantify, however, geochemical tracers are well suited to address this gap (Burnett and Dulaiova, 2003; Burnett et al., 2008; Lecher et al., 2016).

![Figure 2.1](image)

**Figure 2.1** A theoretical mass balance model of water to estimate SGD in a bay with one river. The orange indicates sources of water, and the blue indicates sinks of water.

2.2 Estimating Flux of Submarine Groundwater Discharge (SGD)

Billions of years ago, during the formation of the earth, many radioactive elements were included in the mix of material that formed the planet. Radioactive elements are unstable and transform into another element at an undiscernible moment and emit radiation as a byproduct. The amount of time required for half the atoms of an element to decay is termed the half-life. Three radioactive elements of interest have survived to this day: $^{235}\text{U}$, $^{238}\text{U}$, and $^{232}\text{Th}$. They each stand at the top of a natural radioactive decay chain and have half-lives of billions of years.

Rn is the only non-metallic element in these decay chains; instead, it is an inert, noble gas that escapes any chemical compound that the parent isotope, Ra, is bonded to. Unlike the metals in the decay chains, Rn does not stick or react with any materials. There are three Rn isotopes, $^{219}\text{Rn}$, $^{220}\text{Rn}$, and $^{222}\text{Rn}$, that each exist in one of the three natural decay chains that start as $^{235}\text{U}$, $^{238}\text{U}$, and $^{232}\text{Th}$, respectively (Fig. 2.2).
Figure 2.2 The portions of the three natural decay chains starting as $^{235}\text{U}$, $^{238}\text{U}$, and $^{232}\text{Th}$ that includes the parent and daughter isotopes of Ra and Rn, useful tracers of groundwater.

Due to the half-life of $^{222}\text{Rn}$ ($t_{1/2} = 3.8$ days) being longer than the half-lives of $^{219}\text{Rn}$ ($t_{1/2} = 3.96$ seconds) and $^{220}\text{Rn}$ ($t_{1/2} = 55$ seconds), $^{222}\text{Rn}$ is almost always detectable in the natural environment. Every $^{222}\text{Rn}$ nucleus will eventually decay through a series of transformations that will release alpha particles (i.e., composite particles consisting of two protons and two neutrons), beta particles (i.e., electrons), or gamma particles (i.e., photons), or a combination of these. Since it is difficult to build beta or gamma radiation detectors that can be portable as well as have low background and high sensitivity, most, if not all, Rn detectors will only detect alpha particles.

2.2.1 The RAD-7 Radon Detector

When an alpha particle emits during decay, energy concurrently releases. The solid-state alpha detector used in this thesis, the RAD-7 (Durridge Co., Inc. RAD-7, RAD AQUA), converts the alpha radiation directly to an electrical signal. Each element and its isotopes release an alpha particle with a different, known amount of energy during decay. This allows the RAD-7 to
distinguish between the different Rn isotopes, old and new Rn, and signal from noise, that lowers the background to almost zero.

The RAD-7 measures the [Rn] in air directly by pulling in samples of air through an inlet filter that excludes the isotopic daughters. Since Rn is the only inert gas in the natural decay chains, any alkaline metal progeny produced by Rn adheres to the filter. Rn is neutrally charged, though its isotopic daughters are positively charged. When the daughter isotopes are produced inside the chamber of the RAD-7, an electric field within the detector attracts the positively charged ions. As these short-lived daughters decay, the RAD-7 amplifies, filters, and sorts the signals from the alpha particles according to the strength of the electrical signal. The conversion of the electrical signal to [Rn] was determined by Durridge using two [Rn] (Durridge, RAD H2O User Manual).

The uncertainties associated with the RAD-7 follow a Poisson distribution, the typical radioactive decay statistic. The alpha decays recorded by the RAD-7 can be considered random, independent events which occur over a specific time interval. If Rn counts were low, the uncertainty would be underestimated, so the standard deviation of [Rn] is

\[ \sigma = 1 + \sqrt{N + 1} \]

Where N was the number of counts detected during the cycle that was being averaged over. If there was a cycle with no detected counts, the uncertainty value was based on a two-sigma, 95 % confidence interval, equivalent to \( \pm 4 \) counts over that cycle. To achieve lower uncertainty, the cycle time was increased. Since the Rn isotopes are the only alpha emitters present as gas, all other alpha emitters were caught by the inlet filter, so the RAD-7 was only dealing with Rn alpha emitters.
2.2.2 Continuous Radon Sampling in the Field

Rn in overlying seawater was monitored by pumping a continuous flow of water through a water-air exchanger. This allowed the Rn gas to emanate from the water into a stream of air recirculated through the RAD-7. It first passed through a desiccant to remove the water particles that would otherwise continue to emanate excess Rn within the instrument (Fig. 2.3).

Figure 2.3 Schematic diagram of the RAD-7 system in the continuous sampling layout. The water enters the system through a submersible pump and is emulsified in a water-air exchanger where the $^{222}$Rn can emanate out before the water leaves the system. The water-air exchanger connects in a closed loop with a desiccant and a RAD-7. A temperature data logger in the water air exchanger gets the in-situ temperature of the water passing through the system. This schematic is modelled after Moore and Arnold (1996).

Once an equilibrium between the Rn in air and the Rn in water was established, a known relationship between the two using the temperature of the water was used (Durridge, RAD H$_2$O User Manual).

$$\frac{[Rn_{water}]}{[Rn_{air}]} = 0.105 + 0.40e^{-0.05027T}$$
Where the left-hand side of the equation was the concentration ratio of water to air, and $T$ was the temperature of the water in °C. To reduce the uncertainty associated with the [Rn] in water from [Rn] in air, the cycle over which the Rn counts was increased.

2.2.3 Discrete Radon Sampling in the Lab

Discrete samples could not contact air during collection and bottles were immediately closed because any contact with air will cause the Rn to degas from the water sample. To detect the [Rn] in a discrete sample of water, the RAD H₂O accessory was required in addition to the RAD-7. A glass frit was inserted to the bottom of the sample which aerated the water and allowed the emanated Rn to enter a closed loop where the RAD-7 counted the alpha decays over 20 minutes (Fig. 2.4).

![Figure 2.4 Schematic diagram of the RAD-7 system in the discrete sampling layout. The discrete sample is in a closed loop with a desiccant and a RAD-7. A glass frit connected to the inflowing air aerates the water sample to emanate the $^{222}$Rn. This schematic is inspired Moore and Arnold (1996).](image)

Between samples, we purged the system with ambient air. A background that will be subtracted from the sample counts was conducted by measuring the air in SNIFF mode for 15
minutes. If the background was too high, a small column of 15g of activated carbon was added to the closed loop, which can remove up to 98% of the remaining Rn.

The extraction efficiency (i.e., the amount of Rn emanated from the water into the air loop as a percentage of the equilibrium) for a 250 mL sample is 94% and there is very little or no temperature effect on the overall measurement. The instrument was calibrated at 20°C, so only extremely cold or hot ambient temperatures would affect the measurement.

The RAD-7 calculated the sample [Rn] in the water by multiplying the air loop [Rn] by a fixed coefficient derived from the volume of air in the closed loop, the volume of the sample, and the equilibrium Rn partition coefficient at room temperature. For a 250 mL sample, the sample volume conversion coefficient was around 4.

The decay correction applied to the sample [Rn] \( (C_{\text{measured}}) \) was dependent on the time elapsed between sample collection and analysis. Samples counted within 24 hours have an increased accuracy.

\[
C_{\text{corr}} \left( \frac{Bq}{m^3} \right) = C_{\text{measured}} \left( \frac{Bq}{m^3} \right) \times e^{\lambda_{222Rn}(s^{-1})t(s)}
\]

Where \( \lambda_{222Rn} \) was the isotope decay constant \( \left( \frac{\ln(2)}{\tau_{1/2}} \right) \) and \( t \) was the time between sample collection and sample analysis.

2.2.4 Mass balance model for \(^{222}\)Rn

The use of the RAD-7 in the field allowed for a continuous measurement to be collected over a given length of time. Therefore, environmental \(^{222}\)Rn measured on the RAD-7 can be used to solve for SGD by creating a mass balance model (Fig. 2.5).
Figure 2.5 A theoretical mass balance model of $^{222}$Rn to estimate SGD in a bay with one river. An inventory, denoted as a box, is the total amount of excess $^{222}$Rn (Bq). The flux of the excess $^{222}$Rn moving from one inventory to another, is given as excess $^{222}$Rn per square meter per unit time (Bq m$^{-2}$ s$^{-1}$). The orange indicates sources of $^{222}$Rn, and the blue indicates sinks of $^{222}$Rn.

The following is a step-by-step process of how SGD was calculated based on the sources and sinks of $^{222}$Rn in a body of water. This method is taken from Burnett and Dulaiova (2003) with slight adaptations.

2.2.4.1 Normalizing the $^{222}$Rn bay inventory

The [$^{222}$Rn] in Jakolof Bay was measured by a RAD-7 deployment. The [$^{222}$Rn] measured in the coastal waters ($R_{n\text{measured}}$) is the $^{222}$Rn present in the water column (excess $^{222}$Rn, $R_{n\text{excess}}$) and the $^{222}$Rn being continuously added to the system due to the decay of its parental isotope, dissolved $^{226}$Ra, present in the water column (supported $^{222}$Rn, $R_{n\text{supported}}$).

To determine the activity of $^{226}$Ra, we sampled the water column a few times over the tidal cycle for Ra using the methods described in section 2.3.1 and 2.3.3.7. Due to the half-life of $^{222}$Rn being much shorter than the half-life of its parental isotope, $^{226}$Ra, we assumed they were in secular equilibrium. This means their concentrations were equal.
The inventory of $^{222}\text{Rn}$ was calculated by multiplying the excess $^{222}\text{Rn}$ by the depth of the mixed layer ($h$). The depth of the mixed layer can be determined by collecting water column profiles using a Conductivity-Depth-Temperature (CTD) instrument. If the density of the water column was uniform, it was assumed that the mixed layer depth was equal to the water column depth. However, if the system was stratified, the depth ($h$) was taken as the depth of the mixed layer by looking for a 0.1 kg m$^{-3}$ change in density.

$$Rn_{inventory} \left( \frac{Bq}{m^2} \right) = Rn_{excess} \left( \frac{Bq}{m^3} \right) \times h(m)$$

The inventory was converted into a flux ($J_{Rn}$) by subtracting the normalized inventory between two timepoints. This gave the flux of $^{222}\text{Rn}$ entering the system over the amount of time between the two designated timepoints. Note, this reduced the timeseries by one observation.

$$J_{Rn} \left( \frac{Bq}{m^2 s} \right) = Rn_{inventory,t2} \left( \frac{Bq}{m^2} \right) - Rn_{inventory,t1} \left( \frac{Bq}{m^2} \right)$$

A final normalization accounts for tidal mixing was calculated by taking the difference in tidal amplitude between the two timepoints, multiplied by the $[^{222}\text{Rn}]$ of the mixing water.

During flood time, an offshore $[^{222}\text{Rn}]$ was used. During ebb tide, the $[^{222}\text{Rn}]$ measured in the bay was used. This correction was added to the $J_{Rn}$ to become the normalized inventory ($J_{Rn}^*$).

Next, the $J_{Rn}^*$ was adjusted by the $[^{222}\text{Rn}]$ sources (river flux and sediment diffusion flux) and sinks (atmospheric gas evasion flux and offshore water flux) in the bay to solve for SGD.
2.2.4.2 River flux ($J_{\text{river}}$)

The flux of $^{222}\text{Rn}$ from the river ($J_{\text{river}}$) influencing the location of the RAD-7 measurement was calculated by assuming the river discharge was spread evenly across the surface of the entire bay. First, the $[^{222}\text{Rn}]$ signal from the river was calculated using the river $[^{222}\text{Rn}]$ ($C_{\text{river}}$), the discharge rate of the river into the bay ($v_{\text{river}}$) and the cross-section of the river ($A_{\text{river}}$).

$$J_{\text{river}} \left( \frac{Bq}{m^2 s} \right) = \frac{C_{\text{river}} \left( \frac{Bq}{m^2} \right) \times v_{\text{river}} \left( \frac{m^3}{s} \right)}{A_{\text{river}} \left( m^2 \right)} \times DF$$

The equation was multiplied by a dilution factor (DF) of the river signal spreading out into the bay ($A_{\text{bay}}$).

$$DF = \frac{A_{\text{river}} \left( m^2 \right)}{A_{\text{bay}} \left( m^2 \right)}$$

Where $A_{\text{bay}}$ was the area cross section of the bay. This term was only used in the mass balance calculation if there was a noticeable freshening in the surface waters. If the river discharge didn’t affect the water measured in the bay, then accounting for it decreases the flux of SGD.

2.2.4.3 Sediment diffusion flux ($J_{\text{diffusion}}$)

An estimate of the $^{222}\text{Rn}$ sediment diffusion was determined experimentally by extracting 80 g of wet sediment from the field site that was then equilibrated with 300 mL of Rn-free water in a sealed container with no airspace. The container was left for at least four weeks to allow for the $^{222}\text{Rn}$ to reach secular equilibrium with its parental isotope, $^{226}\text{Ra}$, that was presumably adsorbed to the sediment.
Concentration ($C_{eq}$) was calculated by dividing the $^{222}$Rn measured in the overlying water by the total volume of water in the flask. $C_{eq}$ was then used to estimate the $^{222}$Rn diffusive flux from the sediment.

$$J_{diffusion} \left( \frac{Bq}{m^2 s} \right) = \sqrt{\lambda \left( \frac{1}{s} \right) D_s \left( \frac{m^2}{s} \right) \left( C_{eq} \left( \frac{Bq}{m^3} \right) - C_0 \left( \frac{Bq}{m^3} \right) \right)}$$

Where $\lambda$ was the decay constant of $^{222}$Rn, $D_s$ was the effective wet bulk sediment diffusion coefficient which has been estimated by Corbett et al. (1997) to be $(6.07 \pm 1.61) \times 10^{-8}$ m$^2$ min$^{-1}$ ($(36.42 \pm 9.66) \times 10^{-7}$ m$^2$ s$^{-1}$), and $C_0$ was the $[^{222}$Rn$]$ in the overlying water at the sediment-water interface measured in the field ($C_{measured}$) multiplied by the calculated sediment porosity ($\phi$).

$$C_0 \left( \frac{Bq}{m^3} \right) = C_{measured} \left( \frac{Bq}{m^3} \right) \times \phi$$

The porosity of the sediment was determined by drying the sediment, packing it into a pre-weighed, volume calibrated test tube, and covering it in deionized water until the water reached the soil surface (Dabrowski et al., 2020). The porosity ($\phi$) was calculated as follows:

$$\phi = \frac{\text{water added (g)}}{\text{density of water} \left( \frac{g}{cm^3} \right) \times \text{volume of soil (cm$^3$)}}$$

It is typical that the sediment diffusion flux is very low in comparison to the other fluxes. Many papers have chosen to ignore this term, but it is good practice to include it in calculations because it is a more accurate representation of the overall flux in a system.
2.2.4.4 Atmospheric gas evasion flux ($J_{\text{atm}}$)

The calculation for the atmospheric gas evasion flux assumed that the water column was generally well-mixed. The total flux of $^{222}\text{Rn}$ to the atmosphere ($J_{\text{atm}}$) depended on the concentration gradient across the air-water interface ($C_w$ was the $[^{222}\text{Rn}]$ in surface water; $C_{\text{atm}}$ was the $[^{222}\text{Rn}]$ in air) and turbulent diffusion (MacIntyre et al. 1995).

$$J_{\text{atm}} \left( \frac{Bq}{m^2s} \right) = k \left( \frac{m}{s} \right) \left( C_w \left( \frac{Bq}{m^3} \right) - \alpha C_{\text{atm}} \left( \frac{Bq}{m^3} \right) \right)$$

The $\alpha$ term is Ostwald’s solubility coefficient for $^{222}\text{Rn}$ in coastal waters, which was calculated using the water temperature ($T$, in Kelvin) and salinity ($S$, unitless).

$$A = \exp[-76.14+120.36 \times \frac{T}{100} + 31.26 \times \ln \left( \frac{T}{100} \right)]$$

$$+ S \left(-0.2631 + 0.1673 \times \frac{T}{100} - 0.0273 \times \frac{T^2}{100} \right) \times \frac{T}{273.15}$$

The solubility of a gas is temperature dependent, with a negative relationship between temperature and $^{222}\text{Rn}$ solubility (Wiesenburg and Guinasso, 1979; Weiss and Price, 1980). Salinity influences solubility through a process referred to as the Setschenow constant where the solubility of gas in seawater is approximately 20 % less than in freshwater (MacIntyre et al. 1995).

The gas transfer velocity constant, $k$, depended on wind speed at 10 m above the water surface ($u_{10}$) and the Schmidt number ($Sc$), which was temperature and salinity dependent. However, the effect of salinity was negligible (Saltzman et al. 1993) and was not included in the following equation,

$$Sc = \frac{0.0086}{10^{-1.59 + \frac{980}{T}}}$$
If wind speed was low, it was assumed that the air flow was adjacent to a solid boundary and that \( k \) was proportional to \( Sc^{-2/3} \), but as the wind speed increased and the flow was adjacent to a fluid boundary, \( k \) was proportional to \( Sc^{-1/2} \) (Csanady, 1990). The \( Sc \) is divided by 600 to normalize the flux for \( ^{222}\text{Rn} \) instead of carbon dioxide due to the difference in diffusivity.

It is calculated as follows (MacIntyre et al. 1995; Turner et al. 1996; Csanady 1990),

\[
k (\frac{m}{\text{day}}) = 0.45 u_{10}^{1.6} \frac{Sc}{600}^{-n}
\]

If \( u_{10} \leq 3.6 \text{m/s} \) then \( n = \frac{2}{3} \)

If \( u_{10} > 3.6 \text{m/s} \) then \( n = \frac{1}{2} \)

If there was no wind, there was still a gas evasion flux. It was controlled primarily by convective motion caused by heat loss (MacIntyre et al. 1995). A conservative estimate for \( k(600) \) was derived by Happell et al. (1993) as \( 0.8 \pm 0.5 \text{ cm hr}^{-1} \). This did not account for currents due to tidal movement which, if considered, would only increase the \( k \) value, therefore increasing the SGD estimate making our estimate conservative.

Therefore, \( k \) was calculated for areas of no wind using the following equation (MacIntyre et al. 1995),

\[
k = k(600) \times \frac{Sc^{-2/3}}{600}
\]

2.2.4.5 Offshore mixing flux \( (J_{off}) \)

The flux of \( ^{222}\text{Rn} \) from mixing with less concentrated offshore water \( (J_{off}) \) was estimated two ways: (1) using the water residence time, \( (\tau) \), or (2) using the negative net flux of \( ^{222}\text{Rn} \) calculated at high tide using the method outlined by Burnett and Dulaiova (2003).
First, \( \tau \) (methods in section 2.3.3) was multiplied with \({}^{222}\text{Rn}\) \(({}^{222}\text{Rn}_{\text{bay}})\) in the bay as an estimate for offshore mixing.

\[
J_{\text{off}} = \tau \times {}^{222}\text{Rn}_{\text{bay}}
\]

Second, a common method established by Burnett and Dulaiova (2003) uses the normalized net inventory fluxes. A net flux of \(^{222}\text{Rn} \) \((J_{\text{net}}\)*) was calculated using all the sources and sinks within the model site:

\[
J_{\text{net}}\)* = J_{\text{Rn}}\) * + J_{\text{atm}} - J_{\text{river}} - J_{\text{diffusion}}
\]

The greatest negative \(J_{\text{net}}\)* value was taken as the offshore mixing term because it is not possible for an aquifer to be a sink of \(^{222}\text{Rn}\). The absolute value of this number was then added to every other flux. This offshore mixing term relied on the assumption that the area experienced strong currents and tides (Burnett and Dulaiova 2003).

This second method by Burnett and Dulaiova (2003) has been in question in recent years by the SGD research community. SGD research is nascent, as such, best practices and approaches widely accepted by the scientific community have yet to be established. This thesis will compare an estimate calculated using both approaches to confirm that the original method by Burnett and Dulaiova (2003) can be employed in Jakolof Bay.

2.2.4.6 Calculating \(^{222}\text{Rn} \) SGD \((J_{SGD})\)

The \(^{222}\text{Rn}\) discharged into the bay via groundwater \((J_{SGD})\) was calculated by applying the sources and sinks to the normalized inventory fluxes (Fig. 2.5).

\[
J_{SGD} = J_{\text{Rn}}\) * + J_{\text{atm}} + J_{\text{off}} - J_{\text{river}} - J_{\text{diffusion}}
\]
2.2.4.7 Converting from $^{222}$Rn SGD to water flux ($\omega$)

To convert the $^{222}$Rn SGD ($J_{SGD}$) to the SGD water flux ($\omega$), porewater [$^{222}$Rn] (Rn$_{excess,PW}$) was measured at ebb tide. We estimated this value by deploying a temporary well, a PVC pipe with holes drilled into the bottom and covered in mesh (0.167 cm). A hole twice as large as the pipe was dug in the ground and after the well was put in place, the hole was filled with chunky gravel that served to filter incoming water. The success of this method is described in section 3.3.2.1.

The water flux was then calculated using the following equation,

$$
\omega \left( \frac{m}{S} \right) = \frac{J_{SGD} \left( \frac{Bq}{m^2S} \right)}{Rn_{excess,PW} \left( \frac{Bq}{m^3} \right)}
$$

2.2.4.8 Uncertainty estimates of $^{222}$Rn-based SGD

The analytical error associated with $^{222}$Rn-based SGD estimates were largely ignored (see Burnett and Dulaiova, 2003; Lecher et al. 2016). The uncertainty due to natural variability is typically much greater than the analytical uncertainty; therefore, studies report the environmental variability between repeated measurements as the main source of uncertainty (Burnett and Dulaiova, 2003; Lecher et al. 2016).

2.2.5 Groundwater as a source of nutrients

To determine the role of groundwater as a source of nutrients, porewater nutrient samples were collected from temporary wells and passed through 0.45 μm nitrocellulose membrane filter and stored frozen in acid-cleaned HDPE bottles, then thawed samples were analyzed at the UAF using a Seal Analytical continuous-flow QuAAtro39 AutoAnalyzer (Armstrong et al., 1967;
Murphy and Riley, 1962; Kerouel and Aminot, 1997). The flux of nutrients from SGD ($J_{nut}$) was calculated by multiplying the SGD (m$^3$ s$^{-1}$) by the nutrient concentration ($C_{nut}$).

$$J_{nut} \left( \frac{\mu mol}{s} \right) = C_{nut} \left( \frac{\mu mol}{L} \right) \times \omega \left( \frac{m}{s} \right) \times 1000 \frac{L}{m^3} \times \text{seepage area (m}^2\text{)}$$

2.3 Partitioning Between Freshwater and Recirculated Seawater in SGD

A salt mass balance was used to estimate the freshwater fraction of SGD in the bay (fresh SGD). This model required bay water residence time, which can be estimated using long- and short-lived Ra isotopes or a tidal prism model.

There are four Ra isotopes: $^{223}$Ra, $^{224}$Ra, $^{226}$Ra, and $^{228}$Ra. The shorter-lived Ra isotopes, $^{223}$Ra ($t_{1/2} = 11.4$ days) and $^{224}$Ra (3.6 days) were used over the longer-lived Ra isotopes, $^{226}$Ra ($t_{1/2} = 1600$ years) and $^{228}$Ra ($t_{1/2} = 5.75$ years), to also make a second independent estimate of SGD due to coastal processes occurring on a scale of days rather than years.

2.3.1 Ra field sampling

Due to the low activities of Ra in the ocean, large volumes of water were collected per sample. To obtain reliable activity estimates in the lab, we obtained samples of greater than 100 L of water to get high Ra count rates with respect to background counts (Moore and Shaw, 2008). In environments with glacial plumes, the samples were prefiltered using acrylic fibers to remove particles that would contaminate the sample with the parent isotope of Ra, thorium (Th).

The Ra was extracted by pumping water through a plastic cartridge filled with 25 g of acrylic fiber coated in manganese oxide (MnO$_2$). The acrylic fiber was used because it has a low Ra blank (Moore 1976). MnO$_2$ was used because it has a large binding surface which can
scavenge dissolved metals from seawater, including Ra but also lead, mercury, copper, zinc, cobalt, and cadmium (Moore 1976). The water was pumped through the fiber at a rate of less than 2 L min\(^{-1}\) to enhance the extraction efficiency.

The extraction efficiencies (\(E_{\text{ext}}\)) of the MnO\(_2\) fibers were determined by putting two cartridges in series and measuring the Ra activity on the first fiber (A) and the second fiber (B):

\[
E_{\text{ext}} = \frac{A}{A + B} \times 100\%
\]

After the extraction, the fibers were rinsed with deionized water to remove salt crystals. The presence of salt crystals during the activity counts in the lab would decrease the instrument efficiency by inhibiting Rn emanation from the fibers which was counted by the instrument (Sun and Torgersen, 1998). The fibers were then dried by wringing them out by hand.

In the fall of 2020, I estimated three \(^{224}\text{Ra}\) efficiencies (Table 2.1). The extraction efficiency did not change substantially depending on the \(^{224}\text{Ra}\) activity or the filter rate. This supported the use of a filtration rate that was < 2 L min\(^{-1}\).

**Table 2.1** The extraction efficiencies of Ra from seawater under varying flow rates (L min\(^{-1}\)) and Ra activities (dpm 100 L\(^{-1}\)).

<table>
<thead>
<tr>
<th>(^{224}\text{Ra} \text{ Activity (dpm 100 L}^{-1})</th>
<th>Filter Rate (L min(^{-1}))</th>
<th>Extraction Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.28</td>
<td>1.81</td>
<td>92.5</td>
</tr>
<tr>
<td>1.06</td>
<td>1.4</td>
<td>89.0</td>
</tr>
<tr>
<td>2.72</td>
<td>1.4</td>
<td>86.3</td>
</tr>
</tbody>
</table>

2.3.2 The RaDeCC Counter

The Delayed Coincidence Counter (RaDeCC) was used to measure activities of the shorter-lived Ra (\(^{223}\text{Ra}\) and \(^{224}\text{Ra}\); Fig. 2.2) on MnO\(_2\) fibers. The UAF RaDeCC consists of four
independent counters that can work simultaneously. The radioactivity that they measure refers to the number of decays that occurs per unit of time (dpm).

A cartridge filled with the Mn-fiber was mounted on the RaDeCC system that counted the gaseous Rn daughter isotope emanating from the fiber. To optimize the Rn emanation efficiency, the Mn-fibers were wetted to a ratio of 0.3 to 1 gram of water to gram of fiber. It should be noted that if the fiber was too wet, Rn escape would be inhibited, but if the fiber was too dry, the recoiling Rn atoms would become embedded in adjacent Mn fiber particles (Kim et al., 2001).

Helium gas, which stripped the Rn daughter isotopes from Ra, was used because (1) the gas’ low density allowed alpha particles to travel a longer distance in the scintillation cell (counting cell) and (2) its differing density to ambient air permitted leak detection in the closed loop by watching the flow meter. If the gas flow was inconsistent, that means there was a leak in the system. Gas flow was regulated so that a residence time of gas in the closed loop was 24.6 s (gas flow was 6 L min⁻¹, helium flow was 3.4 L min⁻¹). This gas residence time allowed the \(^{220}\text{Rn}^{216}\text{Po}\) and \(^{219}\text{Rn}^{215}\text{Po}\) pairs to sufficiently decay in the counting cell (Fig. 2.6).
**Figure 2.6** A schematic diagram illustrating the RaDeCC system layout and a flowchart demonstrating how the counts area allocated to bins. The cartridge is in a closed loop with the counting cell, a flow meter to maintain the rate, and an air pump. The first detection window counts the $^{219}$Rn decays associated with $^{223}$Ra. The second detection window counts the $^{220}$Rn decays associated with $^{224}$Ra. If there are too many $^{222}$Rn decays, then the background for the second window is too high so the total count bin is used. This approach was adapted from Moore and Arnold (1996).

When an alpha particle was detected in the counting cell, the first window opened for 5.6 ms (3 half-lives of $^{215}$Po) so if a second count was detected in this window of time, it was likely $^{215}$Po decayed from $^{219}$Rn. This count was tallied in the $^{219}$Rn bin (cpm 219) (Fig. 2.6). After this first window closed, another one opened for 600 ms (4 half-lives of $^{216}$Po) and a count during this time was tallied in the $^{220}$Rn bin (cpm 220) because it was likely $^{216}$Po decayed from $^{220}$Rn (Fig. 2.6). Any count detected in the counting cell – whether or not it was also counted in the 219 or 220 window, was tallied in the total counts bin (cpm total) (Fig. 2.6). These data were collected as counts measured over a discrete time period and was corrected for by using a series of stepwise equations to be converted to activities.
2.3.2.1 Quantification of $^{223}\text{Ra}$ and $^{224}\text{Ra}$ measured through the RaDeCC

The counts measured on the RaDeCC, recorded as counts per minute (cpm), was converted to isotopic activity using a series of stepwise equations (Garcia-Solsona et al., 2008). The resulting activity was reported in decays per minute per liter of water (dpm L$^{-1}$).

The first correction applied to the raw data was due to the spurious counts that occurred when the circuits opened for either bin. These chance coincidence counts (CC) were determined using an equation derived by Giffin et al. (1963).

$$CC = \frac{(cpm_{total} - cpm_{220} - cpm_{219})^2 t_{window}}{1 - (cpm_{total} - cpm_{220} - cpm_{219}) t_{window}}$$

The $t_{window}$ term was the time the count window is open. For the CC$_{220}$ calculation, the $t_{window}$ was 0.01, and for the CC$_{219}$ calculation the $t_{window}$ was $9.3 \times 10^{-5}$. In subsequent usage of this equation, Moore determined that for the CC$_{219}$ calculation, it was more appropriate to use the corrected 220 (corr$_{220}$) than the cpm$_{220}$, which was found by subtracted the chance coincidence from the original counts (Garcia-Solsona et al., 2008).

$$corr = cpm - CC$$

The final correction to the raw data was made due to further cross talk between the channels. The $^{220}\text{Rn}$ bin counted additional decays if two $^{219}\text{Rn}$ decays occurred while the 220 window was open, thereby the second $^{219}\text{Rn}$ decay was recorded in this channel as a $^{220}\text{Rn}$ decay.

$$cpm_{220, final} = corr_{220} - \frac{(1.6 \times corr_{219})^2 \times 0.01}{1 + (1.6 \times corr_{219})^2 \times 0.01}$$

Additional counts were registered in the $^{219}\text{Rn}$ bin because the gate was open long enough for 2.55% of the $^{220}\text{Rn}$ to decay.

$$cpm_{219, final} = corr_{219} - (corr_{220} \times 0.0255)$$
The activity, in decays per minute (dpm), of an isotope was calculated by dividing the final cpm by the efficiency (E) of the counter on which it was recorded.

\[ \text{dpm} = \frac{\text{cpm}_{\text{final}}}{E} \]

The efficiency of a channel was determined by running a standard with known activity many times on the counter between sample measurements. The raw data from the standard counts were corrected using the equations above, before being converted to efficiencies. The efficiency of $^{219}\text{Rn}$ accounts for the decay of $^{227}\text{Ac}$ from the standard preparation because its half-life is 21.8 years, so its activity was altered from the date of standard preparation. The same was not done for $^{232}\text{Th}$, due to its long half-life ($t_{1/2} = 14$ billion years).

\[ E_{219} = \frac{\text{cpm}_{219,\text{final}}}{\text{dpm}_{227\text{Ac,stand}}} \times e^{-\lambda_{227\text{Ac}}t} \]

The dpm$_{227\text{Ac,stand}}$ was the known activity of the standard, $\lambda_{227\text{Ac}}$ was the decay rate for $^{227}\text{Ac}$, and $t$ was the time that has elapsed between the preparation of the Mn-fiber standard and the counting of the standard on the RaDeCC.

\[ E_{220} = \frac{\text{cpm}_{220,\text{final}}}{\text{dpm}_{232\text{Th,stand}}} \]

The dpm$_{232\text{Th,stand}}$ was the known activity of the standard.

The activity of $^{223}\text{Ra}$ was given as the dpm$_{219}$ and the activity of $^{224}\text{Ra}$ was the dpm$_{220}$. However, the activity of $^{224}\text{Ra}$ was also calculated using the total counts channel. The total counts channel registered more than the 219, 220 and background counts so it was not the same number as the calculation with the 220Rn bin. When there was a high amount of $^{226}\text{Ra}$ on the fiber, the total count bin received more counts from $^{222}\text{Rn}$. To determine whether dpm$_{220}$ or dpm$_{220,\text{tot}}$ was used the activity of $^{224}\text{Ra}$, the following ratios were calculated,
If $a$ was much smaller than $b$ the total counts channel was used to calculate the $^{224}$Ra activities because the coincidence events mimicked a high background and the chance coincidence correction for the 220 channel was too high. The cpm of the total counts bin ($cpm_{tot}$) did not require the chance coincidence count or crosstalk corrections. The dpm of the total counts bin was determined from the equations below:

$$dpm_{220,tot} = \frac{(cpm_{tot} - cpm_{tot,bkg})}{E_{total}} - dpm_{219}$$

$$E_{tot} = \frac{cpm_{tot} - cpm_{tot,bkg} - 2 \times cpm_{219}}{dpm_{232Th,stand}}$$

### 2.3.2.2 Preparation of standards and system efficiency

The efficiency of the standards was subdivided into three categories: the system efficiency, the emanation efficiency, and the cell efficiency (Sun and Torgerson 1998).

To determine the system efficiency, standards were made with a known activity of $^{223}$Ra and $^{224}$Ra. $^{224}$Ra decays from $^{228}$Th which has a half-life of 76,000 years so the standard can be used for a long time. However, $^{223}$Ra decays from $^{227}$Th which has a short half-life of 18.7 days. Therefore, the parent of $^{227}$Th, $^{227}$Ac, is used as the standard. It has a half-life of 21.8 years which is why the time of preparation of the standard was required in calculating the counter efficiency because its activity decreased appreciably over time.

The standard was measured before, during, and after counting samples. The resulting system efficiencies were analyzed using a factorial ANOVA after ensuring the assumptions for the test were met. There were no significant interaction terms, but the location and the year were significant factors for system efficiency ($p = 0.035$ and $p = 0.042$, respectively) (Fig 2. 7).
Figure 2.7 A boxplot showing the results of an ANOVA that indicates that the year and location affected the system efficiency.

2.3.3.3 Activity corrections since sample collection

Between sample collection and running the fiber on the RaDeCC, the Ra isotopes decayed. To correct for this loss of activity, we applied the decay rates. \( \lambda_{223} \) and \( \lambda_{224} \) were the decay rates of \(^{223}\text{Ra}\) and \(^{224}\text{Ra}\), respectively.

\[
dpm_{219,\text{corr}} = \frac{dpm\ 219}{e^{-\lambda_{223}t}} \\
dpm_{220,\text{corr}} = \frac{dpm\ 220}{e^{-\lambda_{224}t}} \\
dpm_{\text{tot,corr}} = \frac{(\text{cpm}_{\text{tot}} - \text{cpm}_{\text{tot,bkg}})}{E_{\text{tot}}e^{-\lambda_{223}t}} - dpm_{219,\text{corr}}
\]

2.3.3.4 Correction for supported radium

Although prefiltering in locations with significant suspended particles removed a lot of the parent isotopes, \(^{227}\text{Th}\) and \(^{228}\text{Th}\), some residual activities adsorbed to the Mn-fiber.
‘Supported Ra’ referred to the additional Ra produced from these parent isotopes. They were subtracted from the initial Ra activity estimated using the stepwise equations above. This provided the ‘excess Ra’ term.

The supported Ra was measured by recounting the Mn-fibers once the excess Ra decayed to < 2% of its original activity. This occurs after 5 half-lives, so after 3 weeks for $^{224}$Ra, and after 2 months for $^{223}$Ra. At that point the $^{223}$Ra and $^{224}$Ra were in secular equilibrium with their parent isotope, allowing the counts measured at this time to be a direct measurement of the $^{227}$Th and $^{228}$Th activities.

$$dpm_{228Th} = dpm_{224Ra,t2} - dpm_{224Ra,t1} e^{-\lambda_{224}t}$$

$$dpm_{227Th} = dpm_{223Ra,t2} - dpm_{223Ra,t1} e^{-\lambda_{223}t}$$

The dpm associated with $t_1$ referred to the activity from when the Mn-fiber was first counted. This was multiplied by the expected decay of the isotope since that measurement to give the residual amount of excess Ra activity that might still be emanating from the fiber. The second count, $t_2$, occurred at secular equilibrium so the residual excess Ra was removed from this activity to give the activity of supported Ra.

The excess Ra activity at the time of sample collection was calculated using the final equation below, where $t$ was the decay time between sample collection and the mid-point of the second sample count.

$$ex^{223}Ra = dpm_{219,dec_corr} - dpm_{227Th} e^{-\lambda_{223}t}$$

$$ex^{224}Ra = dpm_{220,dec_corr} - dpm_{228Th} e^{-\lambda_{224}t}$$ or

$$ex^{224}Ra = dpm_{tot,dec_corr} - dpm_{228Th} e^{-\lambda_{224}t}$$
2.3.3.5 Calculation of uncertainties

Since the alpha decays recorded by the RaDeCC were considered random, independent events which occurred over a specific time interval, the data followed a Poisson distribution. $N$ was the number of counts recorded during the count time, so the probability of $N$ counts occurring ($P(N)$) were written as,

$$P(N) = \frac{\bar{N}^N}{N!} e^{-\bar{N}}$$

where $\bar{N}$ was the average number of counts ($N$) that were registered during the time interval. According to a Poisson distribution, the expected value of $N$ (i.e., the mean, $\bar{N}$) and its variance were equal to $\bar{N}$. Therefore, the mean and the standard deviation of each counting measurement was written as $\bar{N} \pm \sqrt{\bar{N}}$, making the percent relative uncertainty ($\Delta_{rel}$) for the raw count data:

$$\Delta_{rel}^{cpm} = \frac{\sqrt{\bar{N}}}{\bar{N}} \times 100 = \frac{\sqrt{N_{corr}}}{N_{corr}} \times 100 = \frac{\sqrt{cpm_{final} t_N}}{cpm_{final} t_N} \times 100$$

Where $t_N$ was the count time. This suggested that the ability to estimate the mean improved (i.e., the relative error decreased) as the number of counts increased. All the samples were counted to a minimum threshold of 400 counts in the $^{220}$Rn bin, which would result in a relative uncertainty of $\leq 5\%$ for $^{224}$Ra. The relative counting errors was only a measurement of the instrument precision, and not an indication of accuracy of the measurement. This method assumed that the distance from the actual activity was relatively small, and the direction of the inaccuracy was in the same direction for all the samples.

The relative counting error was propagated through all the remaining processing steps. The law of uncertainty propagation for uncorrelated variables followed,

$$f(x, y) = \sqrt{\left(\frac{\partial f}{\partial x}\right)^2 \Delta x^2 + \left(\frac{\partial f}{\partial y}\right)^2 \Delta y^2}$$
Where \( x \) and \( y \) were uncorrelated variables acted on by the function, \( f \). The absolute error was represented by \( \Delta \). This formula was applied to most of the processing steps to calculate the absolute counting errors associated with that calculation. The absolute counting errors of each bin followed,

\[
\Delta \text{cpm} = \text{cpm} \times \Delta_{\text{rel} \text{cpm}}
\]

\[
= \frac{N}{t_N} \times \frac{\sqrt{N}}{N} = \frac{\sqrt{N}}{t_N}
\]

Where \( N \) was the uncorrected raw counts. Subsequent steps took into account the independent chance-count and cross-talk corrections.

\[
\Delta CC
\]

\[
= \sqrt{\Delta \text{cpm}_{\text{tot}}^2 + \Delta \text{cpm}_{219}^2 + \Delta \text{cpm}_{220}^2}
\]

\[
+ \frac{(2 \times t_{\text{window}} \times (\text{cpm}_{\text{total}} - \text{cpm}_{220} - \text{cpm}_{219})) - (t_{\text{window}} \times (\text{cpm}_{\text{total}} - \text{cpm}_{220} - \text{cpm}_{219}))^2}{(1 - t_{\text{window}} \times (\text{cpm}_{\text{total}} - \text{cpm}_{220} - \text{cpm}_{219}))^2}
\]

Where the \( \Delta CC_{219} \) used \( \Delta \text{cpm}_{220_{\text{corr}}} \) instead of \( \Delta \text{cpm}_{220} \). The rest of the error term calculations followed the suggested errors from Garcia-Solsana et al. (2008) using propagation of errors.

2.3.3.6 Quantification of \(^{226}\text{Ra} \) and \(^{228}\text{Ra} \) using gamma spectrometry

Fibers were prepared for gamma spectrometry analysis by drying at 300°C for 3 hours, then heating at 800°C for 10 hours (Charette et al., 2001). A piece of paper was placed in the oven with the samples and its absence indicated that carbonization occurred. The fibers were ground almost immediately after removal from the oven to reduce the amount of water absorbed as it cooled.
The mortar was weighed before and after grinding to determine the percent loss of ash from this process. The ash was sealed in a tin container to allow the Ra isotopes to equilibrate with their decay products. The isotope needing the most time was $^{226}\text{Ra}$, which required 5 half-lives of $^{222}\text{Rn}$ (approx. 21 days) to allow the $^{214}\text{Bi}$ to equilibrate with $^{226}\text{Ra}$ (Table 2.2).

Table 2.2 The ideal progeny of radium isotopes with energy peaks that can be detected above background on a gamma spectrum. The days required to equilibrate is five times the half-life of the parental isotope.

<table>
<thead>
<tr>
<th>Radium Isotope</th>
<th>Equilibrated Progeny</th>
<th>Days to Equilibrate</th>
<th>Energy Peak (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{226}\text{Ra}$</td>
<td>$^{214}\text{Bi}$</td>
<td>21 days</td>
<td>602</td>
</tr>
<tr>
<td>$^{228}\text{Ra}$</td>
<td>$^{228}\text{Ac}$</td>
<td>2 to 3 days</td>
<td>911</td>
</tr>
<tr>
<td>$^{224}\text{Ra}$</td>
<td>$^{212}\text{Pb}$</td>
<td>3 days</td>
<td>352</td>
</tr>
</tbody>
</table>

Gamma-ray spectroscopy determined the identity of a radioisotope by comparing the measured energy to known energies of gamma decays. When a nucleus underwent gamma decay it produced a daughter nucleus in an excited state. As it decayed to a lower energy state, a photon was released with a discrete nuclear energy. A high-purity germanium crystal within the instrument converted the gamma radiation into an electrical pulse that was visualized as a peak on the gamma-ray spectrum.

The counts related to the photons detected on the gamma spectrometer were converted to decays of Ra isotope per liter of water through a series of equations. The decays of the progeny were assumed to be the same as the Ra isotope because they were in equilibrium at the time of analysis. The background due to the instrument was calculated by taking three bins before and after the peak as the average background and which fit a Gaussian over the peak. The area within the Gaussian was the net counts that were used in the following calculations.
After a photon hit the crystal and an electrical pulse registered, there was a delay before another photon could be detected. The amount of time that the crystal detected incoming photons was referred to as the live time.

\[ cpm = \frac{\text{counts}}{\text{live time}} \]

A background ashed fiber was run to determine which peaks were due to the fiber \((cpm_{\text{bkgd}})\), and which are due to the elements adsorbed to the fiber \((cpm_{\text{sample}})\).

\[ cpm_{\text{net}} = cpm_{\text{sample}} - cpm_{\text{bkgd}} \]

The decay per unit volume of water sample was then be calculated by

\[ \text{dpm/L} = \frac{cpm_{\text{net}}}{AL \times DE \times BR \times vol_{\text{sample}}} \]

where \(vol_{\text{sample}}\) is the volume of water passed through the fiber in the field, and the three additional factors were as follows

1. Ash Loss (AL): The amount of fiber lost from the ashing process was determined by weighing the mortar empty and after the fiber was ground and removed.

2. Detector Efficiency (DE): For every peak, there was a different detector efficiency. At lower energies and higher energies, the gamma spectrometer had a lower efficiency in its ability to register photon counts.

3. Branching Ratio (BR): During gamma decay, the parent isotope produced one daughter nucleus and two gamma photons. The branching ratio was the rate constant of the production of the daughter nucleus to the rate constant to produce all the particles generated from gamma decay.
Apart from $^{226}$Ra, since it had a half-life of 1600 years, a decay correction was applied to the other Ra calculations. With $t$ being the time between the sample collection and count date and $\lambda$ being the decay rate of the given radium isotope, the excess Ra was

$$ex\ Ra = \frac{dpm}{L} e^{-\lambda t}$$

The uncertainty associated with this value was calculated using propagation of errors. The original error for the net counts on the gamma spectrum was the excess area under the Gaussian created to determine the instrument background. The greater the counts for a peak, the lower this error became. The propagation of this error was the same as described above in section 2.3.3.5.

2.3.3.7 Replicates and Intercalibrations

In Ra studies, replicates were seldom taken due to the water and time constraints in the field. However, the IAEA-Environment Laboratories, Monaco, prepared reference materials (Scholten et al. 2010) so that a RaDeCC system laboratory performance test between laboratories in Europe, Asia, Australia, South America, and North America could be carried out.

The $^{224}$Ra activity on the fibers was stable but the $^{223}$Ra fiber activity decreased for an unknown reason for approximately 6 months after the preparation, after which it reached a relatively stable activity (Scholten et al. 2010). There is still disagreement with the $^{227}$Ac stock used to prepare the solutions, which will affect the activities of $^{223}$Ra.

In February 2021, we received three standards and counted them on the RaDeCC at UAF: C, G, and E. The standards were counted on each of the four counters four times, and the efficiencies of the counters were evaluated using our standard. The performance of the RaDeCC
counters at UAF were assessed following the results of counts of the same standards summarized by Charette et al. (2012).

Table 2.3 University of Alaska Fairbanks RaDeCC performance results for $^{224}$Ra and $^{223}$Ra analysis performed on all four counters. The activities are reported in units (dpm $100L^{-1}$) all reporting a standard deviation except for the reported activity. The standard deviation of the UAF counters were based on the number of the repeated counts ($n = 4$) and the standard deviation for the interlab mean is the reported 12 values of the different labs that were reported by Charette et al. (2012).

<table>
<thead>
<tr>
<th>Standard</th>
<th>Reported Activity</th>
<th>Counter 1</th>
<th>Counter 2</th>
<th>Counter 3</th>
<th>Counter 4</th>
<th>Interlab Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^{224}$Ra</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IAEA-C</td>
<td>14.64</td>
<td>13.21 ±</td>
<td>13.25 ±</td>
<td>12.03 ±</td>
<td>12.99 ±</td>
<td>14.69 ±</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.31</td>
<td>0.38</td>
<td>0.45</td>
<td>0.13</td>
<td>2.24</td>
</tr>
<tr>
<td>IAEA-G</td>
<td>11.10</td>
<td>8.97 ±</td>
<td>8.89 ±</td>
<td>8.05 ±</td>
<td>8.98 ±</td>
<td>10.45 ±</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.28</td>
<td>0.19</td>
<td>0.23</td>
<td>0.57</td>
<td>1.06</td>
</tr>
<tr>
<td></td>
<td>$^{223}$Ra</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IAEA-C</td>
<td>2.310</td>
<td>1.27 ±</td>
<td>1.44 ±</td>
<td>1.33 ±</td>
<td>1.35 ±</td>
<td>1.98 ±</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.05</td>
<td>0.07</td>
<td>0.07</td>
<td>0.18</td>
<td>0.43</td>
</tr>
<tr>
<td>IAEA-E</td>
<td>10.180</td>
<td>3.84 ±</td>
<td>4.01 ±</td>
<td>3.82 ±</td>
<td>3.71 ±</td>
<td>7.33 ±</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.20</td>
<td>0.19</td>
<td>0.26</td>
<td>0.23</td>
<td>1.56</td>
</tr>
</tbody>
</table>

Before standards were analyzed, the voltages of counter 1 through 4 were 812 mV, 673 mV, 536 mV, and 573 mV, respectively. The UAF counters were substantially lower than the interlab mean, illustrating that the values derived from this instrument were underestimated relative to other labs around the world.

2.3.3 Estimating water residence time for the fresh SGD calculation

Water residence time was estimated in two ways: Ra isotopes and a tidal prism.
2.3.3.1 Ra-based water residence time

As elements are introduced from groundwater, they are immediately diluted. By comparing a shorter-lived Ra isotope to a longer-lived Ra isotope, the dilution factor can be ignored since both isotopes are diluted on in the same manner. Instead, the difference in the ratio of activities can be used to determine the time elapsed since that parcel of water left a land-ocean boundary as their half-lives differ (Fig. 2.8).

Figure 2.8 A theoretical mass balance model of Ra to estimate water residence time in a bay with one river. Residence time is estimated using the ratio of a longer-lived Ra (228/226Ra) to a shorter-lived Ra (224Ra). An inventory, denoted as a box, is the total amount of excess Ra (dpm L⁻¹). The flux of the excess Ra moving from one inventory to another, is given as excess Ra per square meter per time (dpm L⁻¹ m⁻² s⁻¹). The orange indicates sources of water, and the blue indicates sinks of water.

By partitioning the bay into smaller reservoirs, the time elapsed from the water entering from the head of the bay to each incremental distance was estimated using the following equation derived by Moore (2000):

\[
\tau = \ln\left(\frac{-Ra_x}{Ra_y}\right)_{initial} \times \frac{1}{\lambda_x - \lambda_y}
\]
Where X was the shorter-lived isotope and Y was the longer-lived isotope. This derivation made the following assumptions:

1. There is one dominant source of radium with constant isotopic composition.
2. The offshore water contains insignificant amount of short-lived radium isotope.
3. The radium isotopes are removed from the bay through mixing and radioactive decay only.

The uncertainty associated with this calculation was derived through a propagation of errors.

If there was continuous advection of SGD across the shoreline of a bay, which is the case in most estuaries and salt marshes, the model from Moore (2006) was applied. It assumed that the system was in steady state, so the additions were balanced by the losses.

\[
\tau = \frac{\left( \frac{Ra_X}{Ra_Y} \right)_{\text{initial}} - \left( \frac{Ra_X}{Ra_Y} \right)_{\text{obs}}}{\left( \frac{Ra_X}{Ra_Y} \right)_{\text{obs}} \times \lambda_X}
\]

The half-life of the longer-lived Ra isotope, Y, was not considered because it was on a much longer timescale than the assumed water residence time. If the ages were expected to be on an order of days, the $^{224}$Ra was used. If the ages were expected to be on an order of weeks, the $^{223}$Ra was used.

2.3.3.2 Water residence time from a tidal prism

Calculating tidal prism required a volume estimate of the bay at high and low tide. This was done by splitting the bay into many slices (Fig. 2.9) and calculating the volume of each slice.
Figure 2.9 Jakolof Bay with the maximum number of slices (40). The red line indicates the length of each slice, adjusted by the purple line when the slice lines aren’t parallel.

This method was adapted from Wang et al. (2015) where triangular elements were constructed within a large bay, however, in Jakolof Bay each slice was assumed to resemble a triangular prism. The depth of the slice was determined by the bathymetry of the bay creating by smoothing out the tidally corrected measurements taken through the repeated seasonal transects of the bay (Fig. 2.10). The average width ($\bar{w}$) of the bay in a slice was calculated by:

$$\bar{w}(m) = \frac{A_{slice} \text{ (m}^2\text{)}}{\ell_{slice} \text{ (m)}}$$

Where $A_{slice}$ was the area of the slice from a bird’s eye view calculated by tracing the perimeter of the slice in ImageJ (https://imagej.net/software/fiji/downloads) and $\ell_{slice}$ was the distance of the slice along the bay (Fig 2.9).
Figure 2.10 The smoothed bathymetry of Jakolof bay using the depths from four 6 station transects, adjusted for tide.

The volume of a slice \(V_{\text{slice}}\) was calculated from:

\[
V_{\text{slice}}(m^3) = \frac{\bar{w}(m) \times \bar{d}(m) \times \ell_{\text{slice}}(m)}{2}
\]

Where \(\bar{d}\) was the average depth of the slice using the depth at the start and end of the slice. The sum of all the slice volumes gave the total volume for Jakolof Bay \(V_{\text{bay}}\). The tidal prism \(P_{\text{tide}}\) was estimated by using the above calculation with the adjusted depths at low and high tide and subtracting them from each other.

Then the water residence time \(\tau\) was:

\[
\tau \text{ (s)} = \frac{V_{\text{bay}}(m^3)}{P_{\text{tide}}/(12 \times 60 \times 60)(m^3/s) + Q_{\text{river}}(m^3/s)}
\]

Where \(Q_{\text{river}}\) was the discharge of the river.
The above steps were repeated with the bay subdivided in different amounts of slices: 1, 5, 10, 20, and 40. The greater the number of slices, the closer the \( V_{\text{bay}} \) and \( P_{\text{tide}} \) estimates became to one another as the numbers converge (Fig. 2.11), and when the bathymetry was changed to add holes or other features that could have occurred between stations in the transect when the depth was originally measured, the uncertainty of the \( V_{\text{bay}} \) remained <4.5 %. Therefore, the 40-slice estimate of the \( V_{\text{bay}} \) and \( P_{\text{tide}} \) were taken, and the associated error is 4.5 % for \( V_{\text{bay}} \) (\( \Delta V_{\text{bay}} \)) and the propagated error for \( P_{\text{tide}} \) (\( \Delta P_{\text{tide}} \)) using:

\[
\Delta P_{\text{tide}} = P_{\text{tide}} \times \sqrt{\Delta V_{\text{bay, high tide}}^2 + \Delta V_{\text{bay, low tide}}^2}
\]

Figure 2.11 The bay volume estimate with a tide of 2.54 m is \( 1.42 \times 10^6 \) m\(^3\) (SD = 31797 m\(^3\), using estimates from slices 5 to 40). Since the bay volume estimates converge with the greater the slices used, the estimate using one slice is not used in the average volume.

Our calculated water residence time was validated by the offshore mixing of \( ^{222}\text{Rn} \) (\( Q_{222\text{Rn, offshore}} \)) using our water residence time estimates,

\[
Q_{222\text{Rn, offshore}} \left( \frac{\text{Bq}}{\text{m}^2 \text{hr}} \right) = \frac{\left[ ^{222}\text{Rn} \right]_{\text{bay}} \left( \frac{\text{Bq}}{\text{m}^3} \right) - \left[ ^{222}\text{Rn} \right]_{\text{offshore}} \left( \frac{\text{Bq}}{\text{m}^3} \right)}{\text{bay depth (m)} \times \tau \left( \text{hr} \right)}
\]
equating to the same term calculated using a $^{222}\text{Rn}$ mass balance (Burnett and Dulaiova, 2003) which did not include the water residence time estimate (91.3 Bq m$^{-2}$ hr$^{-1}$ and 91.1 Bq m$^{-2}$ hr$^{-1}$, respectively).

2.3.4 Estimating the submarine fresh groundwater flux (fresh SGD)

Fresh SGD was estimated across a tidal cycle by using the hourly CTD profiles taken from the zodiac mooring (Fig. 3.7). The top 1 m of salinity data from each water column profile was removed to take out the appearance of a freshwater plume that could be resulting from river discharge because below this section, salinity increased from the sediments upward. This exclusion permitted a more conservative fresh SGD estimate. Then the following steps were fashioned after the total SGD calculation in Burnett and Dulaiova (2003).

1. The average salinity was normalized to the mean tidal height to remove the effect of changing freshwater inventory due to tidal height variations. This was calculated by multiplying the averaged salinity by the depth (excluding the top meter of the water column since the surface of the water was removed in the salinity data).

2. The net flux of salinity entering the water column ($Q_{\text{sal,FSGD}}$) was the change in salinity from one timepoint to another. This was calculated from:

$$Q_{\text{sal,FSGD}(\text{cm/day})} = \frac{d(m)}{\tau \text{ (days)}} \times (1 - \frac{S_{t2}}{S_{t1}}) \times \frac{100 \text{cm}}{m}$$

where,

$d$ = depth was the average depth between one hour ($t_1$) and the next ($t_2$)

$S$ = averaged salinity of the water column during consecutive timepoints, not including the top 1 meter ($t_1$ and $t_2$).
3. The mixing loss correction considered the flux of fresh water mixing with saltier offshore water. As the flux of FSGD is perpetual, even when low, there cannot be a negative flux of FSGD. So, in a well-mixed bay like Jakolof Bay, the offshore mixing flux can be equated to the largest negative net flux (Burnett and Dulaiova, 2003; Burnett et al., 2008).
2.4 References


Chapter 3 The Role of Submarine Groundwater Discharge to the Input of Macronutrients within a Macrotidal Subpolar Estuary

3.1 Abstract

The sources of macronutrients (nitrate, phosphate, and silicic acid) in Jakolof Bay, Alaska are submarine groundwater discharge (SGD), rivers, and offshore water. We estimated SGD using natural geochemical tracers (radon and radium), a salt mass balance, and a two-component salinity mixing equation based on the change in groundwater salinity on an ebb tide. Previous studies have hypothesized that the major macronutrient inputs into Jakolof Bay are rivers and offshore water. The relative contribution of SGD to macronutrient inputs could be significant, particularly within such an enclosed bay with low river discharge. We found that SGD was tidally driven, with a flux of $596 \pm 85$ cm day$^{-1}$ at low tide and $97 \pm 83$ cm day$^{-1}$ at high tide. Ten to twenty-three percent of SGD was freshwater with the rest composed of recirculated seawater. SGD and offshore water contended as the primary sources of nitrate (30 % and 70 % in spring, and 60 % and 40 % in summer, respectively), the limiting nutrient in coastal seawater, while SGD dominated the input of silicic acid. Conversely, the aquifer was a sink for phosphate indicating that the nutrient was primarily sourced from offshore water.$^{1}$

3.2 Introduction

Groundwater (GW) discharge is a dominant pathway for land-derived materials entering the ocean. Globally, GW discharge (fresh and saline) is three to four times greater than the discharge of rivers (Kwon et al., 2014) and transports more nutrients to coastal ecosystems than

$^{1}$Aside from minor alterations to the wording, this chapter consists of a manuscript by Haag, Dulaiova, and Burt (in prep) entitled The Role of Submarine Groundwater Discharge to the Input of Macronutrients within a Macrotidal Subpolar Estuary under review with Marine Chemistry.
rivers in many local studies, for example, the South Sea of Korea (Kim et al., 2003), the Mediterranean (Rodellas et al., 2015), and the nearshore waters off South Carolina (Crotwell and Moore, 2003; Krest et al., 2000), Brazil (Niencheski et al., 2007), the Philippines (Taniguchi et al., 2008), China (Zhang et al., 2020), and Hawaii (Dulai et al., 2016). This flow of water from an aquifer to the sea, regardless of fluid composition (relative ion concentration, e.g., fresh, brackish, or saline) or driving force, is termed submarine GW discharge (SGD) (Burnett and Dulaiova, 2003). The fresh fraction of SGD (fresh SGD) is meteoric water originating as atmospheric precipitation that percolates into the water table and is driven to the ocean by a hydraulic gradient accounting for ~1% of the global freshwater flux to the ocean. As well, over 99% of total SGD is recirculated seawater (saline SGD) driven by oceanic processes such as wave pumping, wave set-up or set-down, and tidal pumping wherein seawater injected into permeable sediments mixes with sediment pore water enriched in dissolved solutes before being drawn back into the ocean (Kwon et al., 2014).

The study of SGD has received increased interest in the last two decades (Moore, 2010; Santos et al., 2021); however, the magnitude and biogeochemical impact of SGD fluxes remain commonly overlooked in nearshore studies. SGD estimates are challenging because they are inconsistent, both spatially and temporally (Burnett and Dulaiova, 2003). Direct measurements using seepage meters can’t account for the small-scale, local variations (Burnett et al., 2001) and hydrological mass balance models don’t account for saline SGD, the largest component of SGD (Kim et al., 2003; Taniguchi et al., 2008; Dimova et al., 2015; Liu et al., 2017). The use of natural geochemical tracers, such as radium (Ra) and radon (Rn), is an effective method to quantify nutrient discharge to estimate total SGD while smoothing out the variation from the heterogeneity of the seepage face (Taniguchi et al., 2019).
Ra concentration can be used as a chemical proxy for SGD due to its conservative nature in seawater and particle reactivity in fresh to brackish environments. As a radioactive alkaline earth metal, the removal terms for Ra in seawater are a product of mixing with less concentrated offshore water coupled with a known decay rate. The four naturally occurring Ra isotopes ($^{224}$Ra, $^{223}$Ra, $^{228}$Ra, and $^{226}$Ra) range widely in half-lives (3.6 days, 11.4 days, 5.8 years, and 1600 years, respectively) and can be used at a variety of oceanographic process timescales (Moore et al., 2003). They are continuously produced by the decay of their parental isotopes ($^{228}$Th, $^{227}$Th, $^{232}$Th, and $^{230}$Th, respectively), which are found primarily in soils, sediments, and rock. The mobility of Ra is restricted in fresh, oxidizing GW due to it being particle reactive in fresh to brackish environments. Ra desorbs from sediments through cation exchange with dissolved ions in seawater that percolates into the aquifer through seawater intrusion (Garcia-Orellana et al., 2021). Ra adsorbs to iron and manganese-oxides formed in oxidizing environments such as sediment modified by redox reactions (Eröss et al., 2012; Lecher et al. 2016a). In coastal waters, noticeable [Ra] indicates water discharged from land or desorbed from suspended or bottom sediments.

Rn, the daughter product of Ra, is more distinguishable from background concentrations in seawater than Ra. Firstly, $^{222}$Rn is an inert noble gas that can build up in porewater and GW but will escape a riverine system through outgassing, thus its detection in marine waters can be linked to a GW source (Eröss et al., 2012; Dabrowski et al., 2020). Secondly, the intrusion of oxygenated seawater into sediments during flood tides precipitates iron- and manganese-(hydr)oxides that are highly efficient at adsorbing Ra (Dulaiova et al., 2008; Lecher et al., 2016a; Eröss et al., 2012); however, whether the Ra is adsorbed to particles or dissolved in GW, it will continually produce Rn. Given these properties, $^{222}$Rn will be more concentrated in GW than Ra.
relative to ambient seawater. The disadvantage of using $^{222}$Rn as a tracer is that its coastal budget must be corrected for atmospheric evasion, at the same time this means that any measured inventories represent recent inputs, that allows for the determination of relatively instantaneous groundwater fluxes (Burnett and Dulaiova, 2003).

The SGD along the coast of the NGA may differ widely. The Alaskan coastline is highly diverse, ranging from rocky to sandy beaches and mudflats, and to varying degrees of exposure to wave action depending on open coastline versus semi-enclosed bays (Field and Walker, 2003). SGD can vary greatly between these locations due to differences in sediment permeability, strength of wave/tidal pumping, and slope of the water table (Virtasalo et al., 2019; Santos et al., 2021). To date, prior SGD work in the NGA has been limited to a partially exposed single rocky beach, where SGD was found to be a significant source of $\text{NO}_3^-$, $\text{Si(OH)}_4^-$, iron, and nickel (Lecher et al., 2016a; 2016b; 2017; Dimova et al., 2015). These studies concluded that Alaskan GW nutrient discharges can rival those of rivers across the entire NGA (Lecher et al., 2016a). However, neither rivers nor SGD are considered the important sources of nutrients to the NGA in summer; instead macronutrients are primarily sourced from offshore topographic steering, eddies, and upwelling (Childers et al., 2005). In semi-enclosed bays, where the degree of advection from offshore water may be limited, SGD is likely to play an enhanced role in supplying macronutrients to the nearshore water. Comparing the relative influence of offshore water to SGD and river input is needed to fully understand the nutrient dynamics in semi-enclosed bays along this coastline.

Since the various SGD tracers are sensitive to different processes and timescales, the quantification of SGD through multiple independent measurements is necessary to validate the robustness of the results. The validation and refinement of Ra-based SGD estimates through
comparison with independent methods such as other tracers, hydrological modelling, and seepage meters (Taniguchi et al., 2008; Kim et al., 2003) is a research need identified in recent reviews of the field (Taniguchi et al., 2019; Garcia-Orellana et al., 2021). Although each technique captures different components of SGD, they integrate over various spatiotemporal scales and are not directly equivalent. Comparisons between independent measurements can lead to differentiation between SGD pathways such as meteoric water discharge, porewater exchange, and tidal flux.

To date, the relative role that tidal pumping has in SGD flux in semi-enclosed bays relative to the overall macronutrient input from advection of oceanic sources is unclear. This study tests the hypothesis that tidally-driven SGD can be a dominant source of macronutrients in a bay with extensive mudflats. Due to the complexity of the nearshore system and SGD pathways, the total SGD estimated from a $^{222}$Rn mass balance model was compared with a Ra mass balance model. The fresh SGD estimated from a salt mass balance model was compared with a two-component mixing equation based on the decrease in GW salinity on an ebb tide. As a critical component of the Ra mass balance, water residence time will be estimated using Ra isotopes and a tidal prism model. SGD estimates will be compared against the site of the only other tracer-based GW study in the NGA, the rocky beach of Kasitsna Bay. We will then compare the relative input of macronutrients to a semi-enclosed from groundwater versus offshore water to understand the relative importance of those sources in shaping the phytoplankton community structure.
3.3 Methods and Materials

3.3.1 Study areas

Jakolof Bay (59.4469°N, 151.5103°W), a semi-enclosed estuary dominated by extensive mudflats (Fig. 3.1), is adjacent to Kasitsna Bay, the site of the only tracer-based groundwater (GW) discharge estimates in the region (Lecher et al., 2016b, Dimova et al., 2015). Both bays possess features that may be conducive to high submarine groundwater discharge (SGD). Saline SGD at these locations is driven by some of the greatest tidal ranges in the world (~8 m), while the fresh fraction is driven by a steep hydraulic gradient created by high mean annual precipitation (450 to 800 mm) and high topographical relief (max elevation = 1140 m, mean elevation = 502 m) (Lecher et al., 2016a). According to Miller and Kelley (2021a), however, the topography in Jakolof Bay suggests minimal fresh SGD, and that porewater intrusion is likely dominated by seawater during flood tide. However, within Jakolof Bay, highly impermeable mudflats, which are composed of roughly 60% fine grained clay and silt (Hartwell et al., 2016), may limit the recirculation of seawater through the sediment and constrict SGD flow to areas of coarser sand.

Unlike most watersheds in Alaska, the heavily forested (64 %) watershed feeding into Jakolof River is small (19 km²) and disconnected from the Harding Ice Field; therefore, the river can dry out by late July after heavy rainfall has stopped and the annual snowpack has melted. The river discharge in this bay is low, ranging between a spring maximum of 2.49 m³ s⁻¹ in late May to zero in August (Jenckes et al., in prep). The source of nutrients in Jakolof Bay presumably varies seasonally, with tidal mixing of advected, seasonally nutrient-rich Alaska Coastal Current (ACC) being the primary origin of macronutrients in spring and autumn (Childers et al., 2005). In the late summer, with little-to-no riverine input, terrestrial nutrients are
likely to be introduced predominantly through SGD. There is physical mixing of the water column in Jakolof Bay throughout the year due to the local wind field controlled by (1) seasonal storm activity in the NGA, (2) daily pressure differentials between the land and ocean, and (3) the flow of cold air from the Harding Ice Field (Field and Walker, 2003). Therefore, the long, narrow bay acts as a wind tunnel that allows for strong overturning of the water column that can distribute nutrients throughout the bay.

3.3.2 Sample collection and analysis

Our field campaign was conducted at neap tide during three seasons: autumn (21 to 25 September 2020), spring (12 to 22 May 2021), and summer (10 to 18 July 2021).

3.3.2.1 GW endmembers from temporary PVC wells

The variability of Ra isotopes and $^{222}$Rn in groundwater (GW) was evaluated by deploying five temporary wells (Lecher et al., 2016b; Krest et al., 2000) in the upper mudflats of Jakolof Bay in spring 2020 (Fig. 3.1). We drilled holes in the bottom foot of a PVC pipe and covered the spaces with mesh (1 mm). During deployment, the diameter of the hole dug in the sediment was at least twice as wide as the width of the well. The space around the well in the two-foot-deep hole was filled with gravel to create larger interstitial spaces for GW to flow, then topped with the removed sediment. The well was wide enough to fit an Onset HOBO conductivity logger, calibrated as seen in Miller and Kelley (2021a), to track the salinity and temperature of the surface aquifer over multiple tidal cycles.
Ra and $^{222}$Rn GW endmembers were collected using a submersible pump. The $^{222}$Rn samples were analyzed using a Rn-in-air monitor (Durridge Co., Inc. RAD-7, RAD AQUA) (Burnett and Dulaiova, 2003). Ra samples (100 L) were pumped from 0.5 m below the surface through a cartridge filled with 25 g of MnO$_2$-coated acrylic fiber at <2 L min$^{-1}$. We placed two cartridges in series to determine our extraction efficiency to be 89% (n = 3). Short-lived $^{224}$Ra was measured in the field on a Radium Delayed Coincidence Counter (RaDeCC) within two days of sample collection and recounted two months later at the University of Alaska Fairbanks (UAF) to correct for the $^{228}$Th supported $^{224}$Ra (Garcia-Solsona et al., 2008; Charette and Buesseler, 2004). The long-lived isotopes, $^{228}$Ra and $^{226}$Ra, were analyzed by ashing the fibers at 800 °C for 10 hours, sealing them for 21 days, and measuring them on a gamma spectrometer at
the University of Hawaii at Mānoa (Charette and Buesseler, 2004). The $^{223}$Ra within seawater was low, resulting in large uncertainties (> 100 %), so this Ra isotope was not used.

To determine the relationship between adsorbed Ra and salinity, we performed a river desorption experiment. On May 14, 2021, five 100 L samples of water from nearby Grewingk River (59.6397°N, 151.1642°W) were taken, and NaCl was added to each sample so that they spanned the following salinities: 0, 5, 10, 15, and 20. As later shown, full desorption of Ra from the riverine suspended particles occurred at salinity 15, so the Jakolof River spring and summer $^{224}$Ra samples were raised to salinity 20 to account for the fraction of the tracer desorbing from riverine suspended solids.

3.3.2.2 Radon and radium measurements in seawater

We calculated total SGD in Jakolof Bay at high and low tide using $^{222}$Rn two ways: (1) a 12-hour mooring from an anchored zodiac from 6:45 to 18:45 on July 17, 2021, using a RAD-7 Aqua, and (2) averaging the $^{222}$Rn inventory from the perimeter of the bay during two zodiac surveys (Fig. 3.1), one at high tide and one at low tide in the spring. The mooring $^{222}$Rn data was integrated over 1-hour intervals to reduce uncertainty to < 10 %. For both methods, a second RAD-7 ran concurrently and measured atmospheric $^{222}$Rn activities. $^{222}$Rn was measured in river and offshore water using the continuous measurement on the RAD-7 Aqua for at least 30 min and river discharge was measured by collaborators (Jenckes et al., in prep). Since the Jakolof Bay mooring could only extend for 12 hours, we included a longer timeseries of $^{222}$Rn that was collected from the Kasitsna Bay dock during September 24 and 25, 2020.

To estimate the seasonal variations in total SGD and water residence time in Jakolof Bay using Ra, we repeated a 6-station transect (Fig. 3.1) during each season. In spring, we conducted
the transect twice: once at high tide and once at low tide. To obtain reliable estimates of Ra, large-volume samples (>100 L) were taken from 0.5 m depth below water surface.

3.3.2.3 Nutrient sampling

Endmember nutrient concentrations were taken from river water, GW, and seawater along the Ra transects at 0.5 m depth below surface in all three seasons (except for GW in autumn). Samples of 20 mL were filtered through a 0.45 μm nitrocellulose membrane filter and stored frozen in acid cleaned HDPE bottles, then thawed samples were analyzed at the UAF using a Seal Analytical continuous-flow QuAAtro39 AutoAnalyzer (Armstrong et al., 1967; Murphy and Riley, 1962; Kerouel and Aminot, 1997). Offshore nutrient concentration estimates were taken from the first station of the historic Seward Line (GAK1) during two cruises: spring 2021 (April 23), and summer 2021 (June 28) (Ana Aguilar-Islas, pers. comm.). We utilized samples taken a month prior to Jakolof Bay fieldwork to compensate for water transit times from GAK1 to our study site. Nutrient data was integrated over the top 75 m of the water column. Monthly nutrient concentrations collected in 2019 from Seldovia Bay, a bay < 10 km from Jakolof Bay (Fig. 3.1), were provided by the NOAA National Estuarine Research Reserve System (2021).

3.3.3 Models and equations

3.3.3.1 $^{222}$Rn mass balance model

The tidal variation in total SGD was calculated using a $^{222}$Rn mass balance model (Burnett and Dulaiova, 2003; Wu et al., 2013). Hourly measurements were taken from a zodiac
over a 12-hour deployment of a RAD-7 Aqua (Rn_measured) and first converted to the normalized inventory (I_net):

\[
I_{\text{net}} = (Rn_{\text{measured}} - Rn_{\text{supported}}) \times d
\]

\[
F_{\text{net}} = I_{\text{net},t2} - I_{\text{net},t1}
\]

where Rn_supported is the ingrowth from \(^{226}\)Ra which is assumed to be in secular equilibrium with its daughter isotope, d is the depth of the mixed layer, and t_1 and t_2 are consecutive timepoints of the timeseries. The F_net must be corrected for other \(^{222}\)Rn sources and sinks contributing to its inventory (F_net\(^*\)):

\[
F_{\text{net}}^* = F_{\text{net}} + /- \Delta d \times Rn_{\text{off/near}} + F_{\text{atm}} - F_{\text{river}} - F_{\text{sed}}
\]

where \(\Delta d\) is the unit change in water depth over the measured interval. If \(\Delta d\) is positive, it is multiplied by the offshore \(^{222}\)Rn activity (Rn_{off}) but if \(\Delta d\) is negative, it is multiplied by the nearshore \(^{222}\)Rn activity (Rn_{near}). The atmospheric gas evasion flux (F_{atm}) is calculated from MacIntyre et al. (1995), using a gas transfer coefficient (k) that accounts for wind speed and air temperature. We measured air temperature from an Omega OM-EL-USB-TC Temperature Logger and wind speed data was taken from Willy Weather (https://wind.willyweather.com/ak/kenai-peninsula-borough/jakolof-bay-airport.html). In the absence of wind, atmospheric evasion does not stop entirely so k is assumed to be 0.8 ± 0.5 cm h\(^{-1}\) (Happell et al., 1993).

The river flux (F_{river}) is equated to the \([^{222}\text{Rn}]\) discharging from the river with discharge data taken from Jenckes et al. (in prep), diluted from the cross-section of the river to the cross-section of the bay. The sediment diffusion flux (F_{sed}) is calculated from a lab experiment where wet sediment is equilibrated with Rn-free water (Corbett et al., 1997; Dabrowski et al., 2020).
The radioactive decay flux is not considered as the hourly fluxes are evaluated on a short timescale relative to the half-life of $^{222}\text{Rn}$ (3.8 days) (Burnett et al., 2008).

Then $F_{\text{net}}^*$ can be converted to SGD flux:

$$SGD = \frac{F_{\text{net}}^* + F_{\text{mix}}}{R_{n_{gw}}} \times \text{seepage face}$$

where $R_{n_{gw}}$ is the greatest measured $[^{222}\text{Rn}]$ in groundwater (1680 ± 150 Bq m$^{-3}$ in spring, 1851 ± 57 Bq m$^{-3}$ in summer; see section 3.3.1) and $F_{\text{mix}}$ is the $^{222}\text{Rn}$ loss via advective mixing with lower $[^{222}\text{Rn}]$ offshore water based on the maximum negative net flux ($F_{\text{net}}^*$). In absence of better estimates, we assumed that this value was valid for the entire measurement period, although tidal currents likely vary. As later shown, this mixing estimate compares well with an independent method from a tidal prism-based water residence time. In spring 2021, the $F_{\text{mix}}$ was calculated using the tidal prism-based water residence time estimate as the $^{222}\text{Rn}$ surveys resulted in only two timepoints:

$$\tau = \frac{V_{\text{bay}}}{Q_{\text{river}} + \left(\frac{V_{\text{bay,high}} - V_{\text{bay,low}}}{\text{time of tidal cycle}}\right)}$$

$$F_{\text{mix}} = \frac{R_{n_{near}} - R_{n_{off}}}{d \times \tau}$$

where $\tau$ is the inner bay’s tidal prism-based water residence time estimate. The primary aquifer through which groundwater will flow in Jakolof Bay are the intertidal mudflats at the head of the bay (Schmoll, 1984) so SGD is constrained within the inner bay (Fig. 3.1). It is calculated using the average volume of the bay ($V_{\text{bay}}$), the discharge of the river ($Q_{\text{river}}$), and the volume of the bay at high and low tide ($V_{\text{bay,high}}$ and $V_{\text{bay,low}}$, respectively) (Wang et al., 2015). Volumes of the bay were estimated by splitting the bay into slices assumed to resemble a triangular prism. The depth of the slice is determined by the bathymetry of the bay created by
smoothing out the tidally corrected measurements taken through the repeated seasonal transects of the bay.

Rn-based advection rate estimates are in units of cm day\(^{-1}\), so to compare this flux to river discharge in units of m\(^3\) s\(^{-1}\), the SGD was multiplied by the seepage face (707,000 m\(^2\)). The seepage face was calculated by tracing the area where most of this flux is likely to occur – the Quaternary surficial deposits at the head of the bay in the intertidal zone (Schmoll, 1984) – and using the average slope of the bathymetry (50°).

The analytical error associated with SGD estimates from \(^{222}\text{Rn}\) concentration measurements is typically considered to be negligible relative to the error due to flux term calculations and natural variability in SGD and endmember concentrations. For this reason, many studies (e.g., Burnett and Dulaiova, 2003; Lecher et al. 2016b, Dulai et al, 2016), report the environmental variability between repeated measurements or a range of SGD that captures extremes in GW endmembers and mixing scenarios. The same approach was employed here.

3.3.3.2 Ra mass balance model

The seasonal variation in total SGD estimates were calculated using a Ra mass balance model where short-lived Ra data were obtained from the RaDeCC system (Garcia-Solsona et al., 2008). Then SGD can be calculated:

\[
SGD = \frac{V_{bay}}{\tau} \left( R_{bay} - R_{off} \right) + \frac{F_{decay} - F_{river} - F_{sed}}{R_{gw}}
\]

where \(\tau\) is the entire bay’s tidal prism-based water residence time. We measured Ra across the entire bay (this tracer is not removed as quickly as \(^{222}\text{Rn}\) that evades the surface water quickly through gas evasion). \(R_{bay}\) is the average [Ra] across the bay, \(R_{offshore}\) is the [Ra] in
offshore water, \( F_{\text{decay}} \) is the radioactive decay flux, \( F_{\text{river}} \) is the river flux whose salinity was increased to 20 to ensure total desorption from the suspended particles (Webster et al., 1995), \( F_{\text{sed}} \) is the sediment diffusion flux calculated using a lab experiment where a layer of sediment of thickness >20 cm was allowed to equilibrate with Ra-free water for one week before the overlying water was measured on the RaDeCC, and \( R_{\text{gw}} \) is the Ra GW endmember (5.2 Bq m\(^{-3}\) in spring, 5.4 Bq m\(^{-3}\) in summer). These conservative Ra GW endmembers represent the \([^{224}\text{Ra}] \) after total desorption (see section 3.4.1). No porewater sample was taken in autumn, thus we used the average \([^{224}\text{Ra}] \) porewater from spring and summer (5.3 Bq m\(^{-3}\)).

Excess Ra is already determined through the RaDeCC measurements, so no further correction for ingrowth from parental isotope from \(^{228}\text{Th} \) is considered.

The seasonal variations in fresh SGD (FSGD) estimates were calculated using a salt mass balance using the CTD profiles taken over the mooring on July 17\(^{th} \), 2021 following a similar set of equations as the total SGD calculated from \(^{222}\text{Rn} \) (Burnett and Dulaiova, 2003; Wang et al., 2015):

\[
F_{\text{SGD net}} = \frac{\bar{d}}{\tau} \times (1 - \frac{S_2}{S_1})
\]

where \( \bar{d} \) is the average depth of the water column over a one-hour interval, \( \tau \) is the water residence time of the inner bay as this mooring was taken near the mudflats at the head of the bay, and \( S_1 \) and \( S_2 \) are the average salinities of the water column between one timepoint and another taken an hour apart. The depth considered above, and its respective salinity, had the top meter of the water column removed so that the freshwater input from the river was not considered in this mass balance. As the presence of the river depends on the tidal cycle, estimating the contribution of the exact river discharge to the upper water column every hour is
difficult. The greatest negative FSGD$_{net}$ is considered the loss of fresh water through mixing with offshore water (FSGD$_{mix}$) and a final FSGD flux was calculated:

\[ FSGD = FSGD_{net} + FSGD_{mix} \]

An independent FSGD estimate was calculated in spring using a two-component mixing equation based on the salinity of porewater from the PVC wells over a tidal cycle (following Dimova et al., 2015).

3.3.3.3 Offshore mixing

The mixing of offshore water with Jakolof Bay was assumed to be driven largely by tides, so it was calculated by dividing the tidal prism based on the change in volume of the bay (Wang et al., 2015) by the tidal cycle (12 hours). The $^{222}$Rn offshore flux was calculated by:

\[ F_{mix} = \frac{R_{n_{bay}} - R_{n_{off}}}{d \times \tau} \]

where $R_{n_{bay}}$ is the $^{222}$Rn in the bay, $R_{n_{off}}$ is the $^{222}$Rn offshore (59.4660°N, 151.5357°W), d is the depth of the water column in the bay, and $\tau$ is the water residence time. In the case of the mooring, the inner bay $\tau$ is used.

The flux of nutrients from offshore water is calculated by multiplying together the tidal prism-based offshore mixing and the concentration of nutrients in offshore water taken as the top 70 m of the water column from the historic Seward Line (59.845°N, 149.467°W) (Table 3.3).

3.3.4 Statistical analysis

We did an autocorrelation in R studio (function acf) to determine the lag between $^{222}$Rn in surface seawater and the tidal amplitude. Following a Shapiro Wilk’s test for normality, significant differences between seasonal nutrient concentrations were determined using an
ANOVA ($p < 0.05$) to determine if at least one season was significantly different from the others. If significance was found, this test was followed by a post-hoc Tukey-Kramer test ($p < 0.05$) to determine which seasonal nutrient concentrations were significantly different from the others. If normality was not found, a Kruskal-Wallis test was used to determine the significantly different seasonal nutrient concentrations. Throughout the text errors associated with estimates are their standard deviations.

3.4 Results and Discussion

3.4.1 GW endmembers

Accurately constraining the spatial and temporal variability of groundwater (GW) endmembers remains a significant challenge in many natural geochemical tracer studies as site specific variability prevents a conceptualization of a formal sampling framework of the aquifer (Garicia-Orellana et al., 2021). Many studies utilize temporary PVC wells to sample GW right before its discharge (e.g., Lecher et al., 2016b; Krest et al., 2000); the extent of the characterization of the GW endmember varies wildly, despite it being a critical component for Ra and $^{222}$Rn mass balances. The [Ra] and $[^{222}\text{Rn}]$ in a subterranean estuary is controlled primarily by changes in salinity and redox conditions (Slomp and Van Cappellen, 2004; Hunter et al., 1998; Dulaiova et al., 2008), that vary with season, pore water depth, distance from shoreline, sediment permeability, and sediment surface chemistry (Dulaiova et al., 2008). As later shown in section 3.4.3, the surficial aquifer of Jakolof Bay was oxic, suggesting that redox conditions were not influencing the GW Ra and $^{222}$Rn endmembers in this system and that the major control over $[^{222}\text{Rn}]$ and [Ra] was GW salinity.
The [\(^{222}\text{Rn}\)] in the aquifer in Jakolof Bay, though heterogeneous, was not controlled by salinity, as observed elsewhere, e.g., in GW in the South Sea of Korea (Kim et al., 2003). In the spring season, the GW [\(^{222}\text{Rn}\)] varied from 489 to 1680 Bq m\(^{-3}\) (average = 947 ± 499 Bq m\(^{-3}\)), with no relationship to salinity (R\(^2\) = 0.0038, n = 7). To ensure more conservative springtime SGD flux estimates, we used the highest measured [\(^{222}\text{Rn}\)] for the spring SGD flux estimates (1680 ± 150 Bq m\(^{-3}\)). This higher value also aligned well with the summertime GW [\(^{222}\text{Rn}\)] measured from a single well (1851 ± 57 Bq m\(^{-3}\)) that was applied for summer total SGD estimates. The range of values measured here compared well with those reported by Dulai et al. (2016) in a wetland in Kaneohe Bay, Hawaii (1500 ± 1300 Bq m\(^{-3}\)), Wu et al. (2013) in the East China Sea (1710 Bq m\(^{-3}\) to 1739 Bq m\(^{-3}\)), and Burnett and Dulaiova (2003) using incubations of nearshore sediment in the Gulf of Mexico (2170 ± 730 Bq m\(^{-3}\)). In contrast, lower GW [\(^{222}\text{Rn}\)] was measured using similar temporary PVC wells at the beach face at Kasitsna Bay (702 ± 103 Bq m\(^{-3}\), Dimova et al., 2015), a second rocky beach < 25 km from Jakolof Bay near the Grewingk River (59.6417°N, 151.1940°W) (366 ± 19 Bq m\(^{-3}\)) and at an Alaskan lake (400 ± 8.3 Bq m\(^{-3}\), Dabrowski et al., 2020). This discrepancy was likely a product of the vastly different substrate, as higher mineral content would contain less of the parent isotope \(^{238}\text{U}\) that produces \(^{222}\text{Rn}\) (Dabrowski et al., 2020). Indeed, the mudflats of Jakolof Bay are formed from unconsolidated fluvial and glacial deposits and the rocky beach at nearby Kasitsna Bay and Grewingk River are poorly sorted greywacke and conglomerate (Bradley et al., 1999; Moxham and Nelson, 1950).

In contrast to \(^{222}\text{Rn}\), a robust linear relationship existed between GW [\(^{224}\text{Ra}\)] and salinity in spring (R\(^2\) = 0.86, n = 7). A river desorption experiment conducted at nearby Grewingk River (Fig. 3.2) showed a linear increase in dissolved Ra with salinity up to a salinity of 15 due to ion-
exchange processes. Similar results were found by Webster et al. (1995) using a lab-based desorption experiment. Using the relationship found here, we estimated the springtime GW Ra endmember to be 5.2 Bq m$^{-3}$. This [Ra] endmember was within the range of values reported by Hancock et al. (2000) for muddy lagoon sediment in Australia at a comparable depth, and the endmember measured at the rocky beach of nearby Kasitsna Bay (2.2 to 3.0 Bq m$^{-3}$, Lecher et al., 2016b).

**Figure 3.2** An experiment using glacial river water and increasing its salinity with NaCl indicated a linear relationship with the desorption of $^{224}$Ra until a salinity of 15 ($R^2 = 0.98$, $[^{224}\text{Ra}] = 0.037 \times \text{salinity} + 0.112$). Total desorption of adsorbed Ra (red) was reached at 15 salinity, so any higher salinity showed the same $^{224}$Ra.

GW salinity changed with the tidal cycle in Jakolof Bay. The salinity in a PVC well increased with flood tide as the STZ between fresh and saline SGD in the aquifer moved landward, then decreased on ebb tide as the STZ moved seaward (Fig. 3.3, Fig. 3.4). However, there was a premature freshwater dip in the salinity during ebb tide before the salinity increased by 5 units (Fig. 3.3), indicating the refilled sediment around the well likely acted as an artificial
conduit for water. As illustrated in Fig. 3.4, at the beginning of the ebb tide the interstitial spaces around the well were filled with overlying seawater, then the freshwater plume from the surface of the bay, and finally saline GW which increased the salinity of the water passing through the well. The salinity at the beginning of flood tide was close to zero, and the salinity of the saline SGD after the premature fresh dip was 18, suggesting a large range of salinity within the discharging GW.

Figure 3.3 The variation in salinity of the GW passing through the temporary PVC wells deployed in the upper mudflat of Jakolof Bay during spring (May) of 2021. The dashed line indicates the height of the tide required for the ground around the well to become submerged. The shaded region is when the tide was greater than this threshold and the ground around the well was submerged. (a) The salinity from one well and the concurrent tidal change. (b) The average salinity during 3 consecutive tidal cycles and the concurrent averaged tidal change (n=3). The slope of the decrease in salinity from these averaged values was used for the fresh SGD estimate according to Dimova et al. (2015).
Figure 3.4 A theoretical diagram depicting the saltwater interface moving landward during the incoming tide and moving seaward during the outgoing tide. While the seawater overlied the hole around the well at high tide, the seawater could percolate into the hole due to the increased permeability of the disturbed sediment when the hole was dug. During the outgoing tide, the seawater filled the hole (blue), then the freshwater plume filled the hole (white), until finally the saline GW could pass through again once the overlying water is gone.

3.4.2 Estimating total and fresh SGD

3.4.2.1 Tidal variation of total SGD using a $^{222}$Rn mass balance

There was variable SGD over a tidal cycle. The proxy for SGD, excess $^{222}$Rn inventory in surface seawater, had a negative correlation with tides in Jakolof Bay and Kasitsna Bay (Fig. 3.5), suggesting an influence from tidal pumping. At low tide, $^{222}$Rn increased due to the steepening of the hydraulic gradient as the sea level subsided. At high tide, $^{222}$Rn decreased as the hydraulic gradient flattened with flood tide and the SGD signal mixed with lower [$^{222}$Rn] offshore water. Similar tidal patterns in $^{222}$Rn have been observed elsewhere (e.g., Burnett and
Dulaiova, 2003; Wu et al., 2013). Also, the lag between low tide and the peak of $^{222}$Rn was greater in Jakolof Bay than in Kasitsna Bay.

Figure 3.5 Variation in total excess $^{222}$Rn (Bq m$^{-3}$) in the ambient seawater with tidal change at (a) Jakolof Bay on July 17th, 2021, and (b) Kasitsna Bay from September 24 to 26, 2020.

This lag between the exfiltration of pore waters on the ebb tide and the signal reaching the moored radon detector was a product of the distance from shoreline, water depth, and topographical conditions (Xin et al. 2011; Wu et al., 2013). While the distance of the RAD-7 Aqua to shore was comparable in both locations, the underlying substrate type in Jakolof Bay is a less permeable mudflat whereas Kasitsna Bay is a rocky beach. A cross-correlation between tidal height and $[^{222}\text{Rn}]$ at Kasitsna Bay yielded a lag of 3 hours. A cross-correlation could not be made for the limited timeseries in Jakolof Bay, so we estimated the lag at the mudflat to be 7 hours using the relationship found at Kasitsna Bay (Fig. 3.5b). We assumed that the greatest $[^{222}\text{Rn}]$ should occur with the lowest tide so the number of hours those two points were displaced from one another indicated the lag. The 7-hour lag in Jakolof Bay compared to the 3-hour lag in
Kasitsna Bay was likely controlled by the permeability of sediment, which can affect the time required for water from the aquifer to reach the seawater surface (Santos et al., 2021).

Total SGD was greater at low tide than high tide in Jakolof Bay (p-value < 0.05). SGD at low tide ranged from 521 to 689 cm day\(^{-1}\) (average = 596 \(\pm\) 85, \(n = 3\)) and at high tide ranged from 0 to 156 cm day\(^{-1}\) (average = 97 \(\pm\) 83, \(n = 8\)) (Table 3.1). The difference in total SGD at low and high tide during summer was 500 \(\pm\) 119 cm day\(^{-1}\), suggesting that total SGD depends on tidal stage throughout the year. The averaged total SGD in summer was 233 \(\pm\) 245 cm day\(^{-1}\) and, in spring, measured from the \(^{222}\)Rn surveys, the averaged total SGD was 241 cm day\(^{-1}\) (Table 3.1; Fig. 3.6), indicating that there was not a significant seasonal difference due to tidal pumping being the primary control over the rate of SGD.
Table 3.1 The total and fresh SGD estimates using independent measurements across various tidal stages and seasons. The reported errors are 1 standard deviation. Total SGD was calculated using conservative estimates of the tracer in GW, but low salinity dominated total SGD was calculated using a $^{224}$Ra sample of salinity in 2.45 spring, 2.6 in summer, and an average of the two for autumn when a porewater sample was not taken.

<table>
<thead>
<tr>
<th>Method</th>
<th>Season</th>
<th>Tide</th>
<th>SGD estimate (cm day$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Total SGD</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Radon</td>
<td>Spring</td>
<td>Entire tidal cycle</td>
<td>241 (n = 2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High</td>
<td>97 ± 83 (n = 8)</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>Low</td>
<td>596 ± 85 (n = 3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Entire tidal cycle</td>
<td>233 ± 245 (n = 11)</td>
</tr>
<tr>
<td></td>
<td>Autumn</td>
<td>Ebb</td>
<td>30 ± 3</td>
</tr>
<tr>
<td>Radium</td>
<td>Spring</td>
<td>Low</td>
<td>10 ± 1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High</td>
<td>14 ± 2</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>Flood</td>
<td>19 ± 3</td>
</tr>
<tr>
<td><strong>Low salinity dominated total SGD</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Radium</td>
<td>Autumn</td>
<td>Ebb</td>
<td>252 ± 28</td>
</tr>
<tr>
<td></td>
<td>Spring</td>
<td>Low</td>
<td>83 ± 11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High</td>
<td>114 ± 15</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>Flood</td>
<td>168 ± 23</td>
</tr>
<tr>
<td><strong>Fresh SGD</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Salt mass balance</td>
<td>Summer</td>
<td>Entire tidal cycle</td>
<td>25 ± 8 (n = 13)</td>
</tr>
<tr>
<td>Well flushing</td>
<td>Spring</td>
<td>Ebb</td>
<td>73 ± 6</td>
</tr>
</tbody>
</table>
Figure 3.6 The $^{222}$Rn surveys conducted at high tide and low tide in Jakolof Bay on May 17th 2021 and May 22nd, 2021, respectively. The depth-corrected $^{222}$Rn inventory was greater on average at low tide than high tide, indicating a higher SGD flux. The change in $^{222}$Rn inventory along one $^{222}$Rn survey was not considered different as the error associated with each measurement was ~50%, however, there was consistency between the maximum $^{222}$Rn inventory geographic locations with tide.

Similar SGD values were observed from a mudflat and rocky beach in the NGA. The SGD in the mudflat in July 2021 ranged across the tidal cycle from 0 to 689 cm day$^{-1}$ (233 ± 245 cm day$^{-1}$, n = 10) and at the rocky beach it averaged 260 ± 360 cm day$^{-1}$ (n = 149) in 2011 and 130 ± 180 cm day$^{-1}$ (n = 145) in 2012 (Dimova et al. 2015). Although the mudflat contains less permeable sediment than the rocky beach, these results indicated that SGD across two disparate substrates were not significantly different, supporting the extrapolation to the entire NGA as done by Lecher et al. (2016a). The high rate of SGD in the Jakolof Bay mudflats could be due to enhanced permeability from seagrass beds (Miller and Kelley, 2021a; Xin et al. 2011) and/or the discrete regions of coarser sediment formed by sediment disturbance from shipping traffic. In the early 20th century, nearby Red Mountain was mined for chrome, in the 1960s and 1970s the bay was logged by the South-Central Timber Company, and in present day gravel is removed from the bay. However, the large variance associated with the averaged SGD over a day indicated that this flux was highly dependent on the tidal stage.
The flux of SGD appeared to be greater in NGA than the global average. Globally, saline SGD dominates total SGD by >99% relative to fresh SGD (Santos et al., 2021) and the tidal range in this region of southcentral Alaska – the primary mechanism driving saline SGD – is among the largest on the planet (Whitney, 2002). This resulted in estimates of total SGD in Alaska one to three orders of magnitude greater than the median SGD rates reported in both the Pacific (2-22 cm day⁻¹) and Atlantic Oceans (1-10 cm day⁻¹) (Santos et al., 2021).

3.4.2.2 Ra- and tidal prism-based water residence times

In solving for SGD, an offshore mixing flux of Ra was needed for the mass balance, which required an estimate of the water residence time. The ratio of a shorter-lived Ra isotope, ²²⁴Ra, to a longer-lived Ra isotope, ²²⁶Ra or ²²⁸Ra, is a commonly used method in nearshore studies to estimate water residence time (Moore, 2000) since the [Ra] is typically one to three orders of magnitude greater in GW than seawater (García-Orellana et al., 2021; Moore, 2000; Zhang et al., 2020; Charette and Buesseler, 2004; Krest et al., 2000; Diego-Feliu et al., 2021). In our study, the [²²⁴Ra] in GW (0.71 ± 0.61 Bq m⁻³, n = 6) was 2 to 3 times greater than seawater (0.29 ± 0.18 Bq m⁻³, n = 27); however, the [²²⁶Ra] in GW (0.34 ± 0.16 Bq m⁻³, n = 2) was 3 to 4 times less than seawater (1.4 ± 0.35 Bq m⁻³, n = 12) and the [²²⁸Ra] in GW (0.14 ± 0.24 Bq m⁻³, n = 2) was comparable to seawater (0.40 ± 0.21 Bq m⁻³, n = 12). Compared to other offshore sites, NGA seawater [²²⁶Ra] (0.34 ± 0.16 Bq m⁻³, n = 12) ranged from comparable to 2 times lower: 1.5 ± 0.04 Bq m⁻³ in South Carolina (Moore, 2000), 3.5 ± 1.1 Bq m⁻³ in China (Zhang et al., 2020), and 2.7 ± 0.42 Bq m⁻³ in Chesapeake Bay (Charette and Buesseler, 2004). However, the Alaskan GW [²²⁶Ra] (0.34 ± 0.16 Bq m⁻³, n = 2) was 2 to 3 times lower than those locations, resulting in a linear increase in seawater [²²⁶Ra] with distance towards the mudflats of Jakolof

81
Bay at low tide in spring and summer ($R^2 = 0.985$ and $R^2 = 0.710$, respectively). This invalidated the assumption that the sole source of Ra isotopes was from the head of the bay required to make an Ra-based water residence time estimate; however, further investigation should be done in other locations in the NGA to determine if this was a site-specific occurrence.

Residence times calculated using a tidal prism method (Wang et al., 2015) yielded values of 0.61 days in September, 0.69 days in May, and 0.69 days in July. The water residence time for the inner half of Jakolof Bay, which encompassed the mudflats, was 0.24 days in September, 0.30 days in May, and 0.31 days in July. Using the residence time of the inner bay in July, the $^{222}\text{Rn}$ offshore mixing estimate was $94 \pm 30 \text{ Bq m}^{-2}\text{ hr}^{-1}$. It was comparable to the value we calculated using the offshore mixing method from Burnett and Dulaiova (2003), 91 Bq m$^{-2}$ hr$^{-1}$, which assumed that this site has strong mixing due to a large tidal range. This showed that the tidal prism provided an accurate estimate of water residence time. Therefore, tidal prism-based water residence time was used in the $^{224}\text{Ra}$ mass balance for the offshore mixing flux.

3.4.2.3 Ra-based Total SGD

The Ra-based SGD estimates were an order of magnitude lower than the $^{222}\text{Rn}$-based SGD estimates in Jakolof Bay discussed above (Table 3.1). Similar discrepancies existed between prior Ra- and Rn-based SGD calculations at the rocky beach at Kasitsna Bay (Lecher et al., 2016b; Dimova et al., 2015). Here, we discuss 5 potential explanations for these discrepancies.

First, the $^{222}\text{Rn}$ GW endmember was measured half a meter into the aquifer, where gas evasion to the atmosphere can be a relevant sink depending on water temperature, salinity, atmospheric pressure and sediment porosity or rock permeability (Barberio et al., 2018). If the
GW endmember [222Rn] was lower due to premature gas evasion, then the Rn-based SGD estimate would be increased. However, we used the greatest [222Rn] measured from GW, likely minimizing this issue.

Second, but less likely for reasons explained below, the 222Rn-based estimate, taken from one stationary location, may have captured a hotspot of SGD, whereas the Ra-based estimate averaged the entire bay. If there wasn’t uniform seepage across the mudflat, and instead there were areas of coarser, more permeable sediment, the heterogeneity in SGD might not have been captured in the 222Rn measurement. It is possible that the SGD was concentrated to these hotspots of coarser sediment and not the entire calculated seepage face. However, the spring 222Rn-based estimate used a survey that averaged the tracer around the entire bay and the resulting SGD estimate was in the same order of magnitude as the stationary one. This suggested that a hotspot wasn’t captured in summer and the estimate was representative of the entire seepage face.

Third, if the seepage face (707,000 m²) was overestimated, then it would result in an underestimate of Ra-based total SGD in units of cm day⁻¹. The Ra-based estimate used the area of the seepage face to get SGD in the units of cm day⁻¹, unlike the 222Rn-based estimates and the salt mass balance for fresh SGD. To make the Ra- and Rn-based SGD estimates agree, the seepage face would have to be an order of magnitude smaller, which would support a patchiness in the mudflat of more and less permeable sediment throughout.

Fourth, 222Rn-based GW estimates accounted for both the fresh and saline SGD pathways, whereas the 224Ra GW estimates were salinity dependent and may be biased to higher salinity. When seawater percolates into the aquifer to recharge saline SGD, Ra tends to desorb from aquifer solids by cation exchange reactions; however, Ra retains its particle reactivity in
fresh SGD and the discharged fresh GW will not have the same enrichment of Ra as the saline GW (Webster et al., 1995; Crotwell and Moore, 2003). Therefore, the difference between $^{222}$Rn and $^{224}$Ra SGD estimates may, to some degree, have revealed the importance of the fresh SGD component, that may not be fully captured by the applied Ra endmember due to variability in GW [Ra] over the tidal cycle.

Fifth, the Ra GW endmember did not represent the salinity of the aquifer (Dulaiova et al., 2008). When the flux of Ra from SGD was divided by the respective endmember, a larger endmember would result in a smaller SGD estimate. If the $^{224}$Ra GW endmember was lower than the one used above, it would increase the SGD flux. We assumed that to make a conservative estimate of GW [$^{224}$Ra], we had to theoretically increase the salinity to 15. But the salinity of the GW ranged from a salinity near 0 up to 18 (Fig. 3.3), implying that at times the SGD could be fresher, and thus contain less [$^{224}$Ra] due to decreased cations exchange. If we instead used the average spring GW [$^{224}$Ra] endmember measured in Jakolof Bay (0.628 Bq m$^{-3}$, average salinity 2.45 (n = 8)), the spring total Ra-based SGD increased to 83 cm day$^{-1}$ at low tide and 114 cm day$^{-1}$ at high tide (Table 3.1). This brought the estimates to similar magnitudes as the Rn-based estimates.

The Ra data in spring showed that there was greater SGD at high tide than at low tide (Table 3.1) that was incongruent with many other studies (Burnett and Dulaiova, 2003; Burnett et al., 2003, Dimova et al., 2015; Kim et al., 2003; Niencheski et al., 2007; Dulai et al., 2016). This could be attributed to a difference in salinity in discharging GW across a tidal cycle. If SGD at high tide was more saline than low tide (Fig. 3.3), the GW [$^{224}$Ra] would not be the same. Using the saline $^{224}$Ra endmember at high tide (5.2 Bq m$^{-3}$) and the fresher $^{224}$Ra endmember at
low tide (0.628 Bq m⁻³), SGD at high tide was 14 ± 2 cm day⁻¹ and SGD at low tide was 88 cm day⁻¹.

However, the relative total Ra-based SGD was greater in summer and autumn than in spring (Table 3.1), contrary to the Rn-based estimates that showed similar fluxes between spring and summer (241 cm day⁻¹ and 233 ± 246 cm day⁻¹, respectively). Lecher et al. (2016b) reported that due to the dominant driving force in this area being tidal pumping, there shouldn’t be significant variations in SGD throughout the year.

3.4.2.4 Fresh SGD estimates

In Jakolof Bay, hourly CTD profiles taken over a tidal cycle revealed what appeared to be a direct observation of SGD (Fig. 3.7). Specifically, a layer of relatively warm, fresh (salinity as low as 25), and oxygen-poor water directly above the seafloor. The magnitude of this fresher signal indicated that fresh/brackish SGD constituted a significant fraction of the total SGD signal. For comparison, Dimova et al. (2015) calculated that fresh SGD at the beach in Kasitsna Bay was 1 % of the total SGD signal. From that study, the seawater had a salinity of 31.2 and assuming a fresh SGD salinity of 0, the total SGD should have a salinity of 30.1. In contrast, the minimum salinity recorded here above the seafloor in Jakolof Bay was 24.99.
Figure 3.7 The water column in Jakolof Bay over a tidal cycle on July 17\textsuperscript{th}, 2021, reveals a water mass above the sediment at low tide characterized by lower salinity, higher temperature and lower dissolved oxygen (red boxes) that is likely SGD.

A salt mass balance applied to the hourly CTD data (Fig. 7) yielded fresh SGD ranging from 18 to 39 cm day\textsuperscript{-1} (24 ± 8 cm day\textsuperscript{-1}, n=12) over the tidal cycle. Therefore, the percent of fresh SGD in summer was ~10 % (Table 3.1). While global total SGD is < 1 % fresh (Santos et al., 2021; Taniguchi et al., 2008), Wang et al. (2015) also measured a fresh to saline SGD ratio as ranging from 7 % to 8.2 % in Laizhou Bay, China. These fresh SGD estimates from Jakolof Bay were 3 orders of magnitude greater than Kasitsna Bay, where fresh SGD made up 1 % of total SGD (Dimova et al., 2015). Calculating fresh SGD at Jakolof Bay using the well flushing method from Dimova et al. (2015) resulted in a fresh SGD estimate of 73 ± 6 cm day\textsuperscript{-1} that was 23 % of total SGD. This estimate considered the flushing of saline to fresh SGD during ebb tide in a well with a diameter of 5 cm in spring, while the salt mass balance considered the freshwater input from the same mooring as the \textsuperscript{222}Rn timeseries in summer (Fig. 3.1) that allows for more smoothing out of local variation. If the Jakolof Bay aquifer was linked to other aquifers in the...
bay with connections to glacierized watersheds, that could explain the presence of a greater flux of fresh SGD entering Jakolof Bay than the rocky beach at Kasitsna Bay.

3.4.3 Dominant inputs of nutrients into Jakolof Bay

The largest sources of nutrients to Jakolof Bay were SGD and offshore water (Table 3.2). The offshore water originated as part of the Alaska Coastal Current (ACC), a buoyancy-driven coastal current that enters Jakolof Bay following bathymetric contours (Stabeno et al., 2004; Field and Walker, 2003). Sambrotto and Lorenzen (1986) suggested that the water outside the mouth of Jakolof Bay was one of the most biologically productive ecosystems in the world due to the high supply of nutrients to surface waters from frequent storms and persistent currents stimulating strong, vertical mixing along the continental shelf. While the offshore water enters at depth and mixes upward, SGD and river discharge typically are lighter than seawater so they will primarily reside on the surface of the bay. Though Jakolof River played a minor role in inputting macronutrients to the nearshore environment (Table 3.2), its discharge was smaller than many nearby glaciated rivers (Jenckes et al., in prep) so the following results comparing relative macronutrient inputs may not be representative for all bays along the NGA coastline. Additionally, this study was unable to capture the variability of offshore mixing of nutrients into the bay over a tidal cycle.
Table 3.2 Nutrient inputs to Jakolof Bay in spring and summer 2021. The seepage face was taken as 707,000 m² which has an associated error of 10%.

<table>
<thead>
<tr>
<th>Source</th>
<th>Water flux (m³ s⁻¹)</th>
<th>NO₃⁻ discharge (mmol day⁻¹)</th>
<th>PO₄³⁻ discharge (mmol day⁻¹)</th>
<th>Si(OH)₄ discharge (mmol day⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>May 2021</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>River</td>
<td>1.1</td>
<td>2.1 ± 0.2</td>
<td>0.004 ± 0.002</td>
<td>9.8 ± 0.9</td>
</tr>
<tr>
<td>Rn-based SGD</td>
<td>20 ± 7</td>
<td>9.4 ± 9.0</td>
<td>0.15 ± 0.13</td>
<td>110 ± 92</td>
</tr>
<tr>
<td>Offshore mixing</td>
<td>24 ± 2</td>
<td>26 ± 12</td>
<td>2.5 ± 1.1</td>
<td>40 ± 18</td>
</tr>
<tr>
<td><strong>July 2021</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>River</td>
<td>0.6</td>
<td>0.52 ± 0.04</td>
<td>0.003 ± 0.001</td>
<td>5.2 ± 0.6</td>
</tr>
<tr>
<td>Rn-based SGD, low tide</td>
<td>49 ± 7</td>
<td>32 ± 15</td>
<td>0.93 ± 0.45</td>
<td>510 ± 200</td>
</tr>
<tr>
<td>Rn-based SGD, high tide</td>
<td>8 ± 6</td>
<td>5.1 ± 4.9</td>
<td>0.15 ± 0.14</td>
<td>82 ± 75</td>
</tr>
<tr>
<td>Offshore mixing</td>
<td>24 ± 2</td>
<td>11 ± 5.0</td>
<td>1.7 ± 0.75</td>
<td>23 ± 10</td>
</tr>
</tbody>
</table>

SGD was constricted to the mudflats, as indicated by the rapid, log-linear declines in

$^{224}$Ra activities with distance from the head of Jakolof Bay (Fig. 3.8). This was similar to the finding for Kasitsna Bay (Lecher et al. 2016b). Therefore, it appeared that chemical alterations to seawater within the mudflat at the head of the bay coupled with strong tidal mixing of offshore water played a major role in the nutrient dynamics of this nearshore system.
Figure 3.8 There was a significant relationship ($p < 0.05$) with the natural log of $^{224}$Ra and distance from the head of the bay. The fitted linear regression had an $R^2$ value of 0.90 in autumn, 0.85 in spring at low tide, 0.78 in spring at high tide, and 0.75 in summer.

3.4.3.1 Nitrate

The dominant sources of the limiting nutrient in Jakolof Bay, $\text{NO}_3^-$, shift from spring to summer. The ratio of $\text{NO}_3^-$ to $\text{PO}_4^{3-}$ was used to identify the limiting nutrient in seawater, assuming the general requirement for phytoplankton approximates the Redfield ratio ($\text{N}:\text{P} = 16$). The $\text{N}:\text{P}$ in Jakolof Bay seawater was $< 10$ throughout the year (Table 3.3), implying that $\text{NO}_3^-$ was the major limiting nutrient. The decrease in seawater $[\text{NO}_3^-]$ from spring to autumn (Dunn test, $p$-value $< 0.05$) reflected seasonal nutrient draw-down. Similar $\text{N}:\text{P}$ ratios were reported in nearby Seldovia Bay (Fig. 3.9) and in offshore NGA water (Childers et al., 2005). While the SGD $\text{NO}_3^-$ flux increased from spring to summer ($9.4 \pm 9.0$ mmol day$^{-1}$ and $19 \pm 16$ mmol day$^{-1}$, respectively), the $\text{NO}_3^-$ flux from offshore mixing was reduced by half ($26 \pm 12$ mmol day$^{-1}$ and
11 ± 5 mmol day⁻¹, respectively) (Table 3.2), shifting the dominant source of NO₃⁻ from offshore mixing of NGA water to SGD from spring to summer.

Table 3.3 The concentration of nutrients in the river, GW, surface seawater, and depth-integrated offshore water across seasons in Jakolof Bay. Offshore water NO₃⁻ is given as NO₃⁻ plus nitrite. GW samples were taken from a temporary PVC well at ebb tide. The associated uncertainty is the standard deviation of the replicates.

<table>
<thead>
<tr>
<th>Source</th>
<th>NO₃⁻ (μM)</th>
<th>NH₄⁺ (μM)</th>
<th>PO₄³⁻ (μM)</th>
<th>Si(OH)₄ (μM)</th>
<th>N:P</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>September 2020</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>River water*</td>
<td>9.95</td>
<td>0.42</td>
<td>0.07</td>
<td>90.51</td>
<td>145.23</td>
</tr>
<tr>
<td>Seawater**</td>
<td>3.50 ± 0.76</td>
<td>0.76 ± 0.08</td>
<td>0.74 ± 0.09</td>
<td>10.00 ± 2.56</td>
<td>4.73</td>
</tr>
<tr>
<td><strong>May 2021</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>River water</td>
<td>22.35 ± 0.27</td>
<td>0.24 ± 0.03</td>
<td>0.04 ± 0.01</td>
<td>108.02 ± 0.88</td>
<td>615.23</td>
</tr>
<tr>
<td>GW</td>
<td>5.50 ± 3.02</td>
<td>0.87 ± 0.28</td>
<td>0.09 ± 0.03</td>
<td>64.74 ± 20.4</td>
<td>63.43</td>
</tr>
<tr>
<td>Seawater***</td>
<td>5.39 ± 1.56</td>
<td>1.08 ± 0.21</td>
<td>0.66 ± 0.16</td>
<td>14.39 ± 3.96</td>
<td>8.17</td>
</tr>
<tr>
<td>Offshore</td>
<td>12.4</td>
<td>1.20</td>
<td>18.9</td>
<td>10.3</td>
<td></td>
</tr>
<tr>
<td><strong>July 2021</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>River water</td>
<td>9.81 ± 0.07</td>
<td>0.39 ± 0.26</td>
<td>0.05 ± 0.01</td>
<td>98.2 ± 1.52</td>
<td>196.20</td>
</tr>
<tr>
<td>GW</td>
<td>7.50 ± 0.68</td>
<td>0.75 ± 0.08</td>
<td>0.22 ± 0.02</td>
<td>119.88 ± 2.44</td>
<td>34.09</td>
</tr>
<tr>
<td>Seawater**</td>
<td>1.43 ± 1.17</td>
<td>1.26 ± 0.28</td>
<td>0.43 ± 0.13</td>
<td>23.94 ± 30.08</td>
<td>3.33</td>
</tr>
<tr>
<td>Offshore</td>
<td>5.28</td>
<td>0.801</td>
<td>10.7</td>
<td>6.59</td>
<td></td>
</tr>
</tbody>
</table>

*No replicates collected in September 2020.
**One replicate collected at each of the 6 stations along the transect in Jakolof (n = 6).
***Transect done at low and high tide (n = 12).
**Figure 3.9** The N:P in Seldovia Bay decreased from winter to late summer in 2019, before increasing in autumn. The three spot samples taken in Jakolof Bay from 2021 and offshore water reported in Childers et al. (2005) follow the same trend.

There was greater regeneration of NO$_3^-$ in GW in summer than spring. In spring, the [NO$_3^-$] in averaged surface seawater and GW were not significantly different (Kruskal-Wallis test, p-value > 0.05), thus [NO$_3^-$] was not enriched in SGD. This indicated that organic matter decomposition in sediments yielded no appreciable enhancement of NO$_3^-$ in GW and NO$_3^-$ was not significantly removed from seawater. In contrast, GW [NO$_3^-$] in summer was enriched relative to seawater (Kruskal-Wallis test, p-value < 0.05), indicating enrichment of NO$_3^-$ in SGD. In other words, SGD only enriched seawater with NO$_3^-$ in summer and not spring.

The presence of relatively high GW [NO$_3^-$] suggested a short residence time in the Jakolof Bay aquifer, which would result in oxic conditions. The [NO$_3^-$] was high in fresh GW (5.50 ± 3.02 µM in salinity of 3.9 during spring and 7.50 ± 0.68 µM in salinity of 0.1 during summer) (Table 3.3). This had been shown in Kasitsna Bay to result from short residence time in
the aquifer (Lecher et al., 2016a). Shallow aquifers with short residence times are typically oxic; whereas in deep aquifers with long residence times, dissolved oxygen is often consumed entirely, leading to declines in porewater [NO$_3^-$] via denitrification (Slomp and Cappellen, 2004; Hunter et al., 1998). Oxic conditions within these mudflats could also point to limited organic matter production within the sediment (Hunter et al., 1998), but the Jakolof Bay mudflats have been shown to be highly productive (Miller and Kelley, 2021b), so the presence of NO$_3^-$ suggested that the residence time in the aquifer was short enough to maintain an oxic environment. Indeed, pore water timeseries data collected throughout June 2019 by Miller and Kelley et al. (2021a) yielded porewater [O$_2$] in the top 10 cm of the sediment between 94 and 562 μM (average = 330 ± 87, n = 67). This suggested that the water residence time of the Jakolof aquifer was short.

3.4.3.2 Phosphate

Within the Jakolof Bay aquifer system, SGD acted as a sink for PO$_4^{3-}$. Seawater [PO$_4^{3-}$] in spring was significantly lower at low tide (0.34 to 0.64 μM) compared to high tide (0.58 to 0.87 μM) but was always considerably higher than GW [PO$_4^{3-}$] (0.09 ± 0.03 μM, Table 3.3). Similar results were found in summer, with seawater [PO$_4^{3-}$] at flood tide ranging from 0.18 to 0.55 μM (0.43 ± 0.13 μM, n = 6) and a GW [PO$_4^{3-}$] of 0.22 ± 0.02 μM (n = 3, Table 3.3). This was likely due to the particle reactive nature of PO$_4^{3-}$, which adsorbs to compounds like aluminum silicates, opal, and iron- and manganese-(hydr)oxides actively formed due to oxic conditions (Nixon, 1980; Chambers and Odum, 1990; Lecher et al., 2016a).

With SGD deemed a PO$_4^{3-}$ sink, the dominant source of this macronutrient to Jakolof Bay was offshore water originating from the ACC. This was supported by the observation of higher seawater [PO$_4^{3-}$] at high tide (i.e., when the signal of offshore water was greater) relative to low
tide (Table 3.3), the [PO$_4^{3-}$] in offshore water being greater than the bay seawater (Table 3.3), and offshore mixing being a greater PO$_4^{3-}$ flux than SGD and river discharge (Table 3.2). It is important to note, however, that the desorption of PO$_4^{3-}$ from riverine suspended solids could represent an additional, yet previously undocumented source of PO$_4^{3-}$ to Jakolof Bay.

The seawater N:P may have suggested an additional source of PO$_4^{3-}$ at the head of Jakolof Bay. The linear increase in N:P with distance from the mudflats (Fig. 3.10) indicated mixing with higher N:P offshore water. The lower N:P at the head of the bay (< 10) was not a result of GW whose N:P ranges from 63.43 in spring to 34.09 in summer (Table 3.3). It was not due to biological uptake or regeneration in the water column as that did not significantly change the N:P. Denitrification, the removal of biologically available nitrogen, was unlikely to occur in oxic, well-mixed seawater. Though the following are the typical explanations for low N:P in coastal water, the oxic conditions in the Jakolof Bay sediment (Miller and Kelly, 2021a) could not induce faster regeneration of PO$_4^{3-}$ relative to NO$_3^-$ in sediment (Nixon, 1980; 1981) because denitrification did not occur to remove NO$_3^-$, and the desorption of PO$_4^{3-}$ from iron- and manganese-(hydr)oxides during reducing conditions in the sediment (Nixon, 1980; 1981) was unlikely due to the aquifer acting as a sink for PO$_4^{3-}$. However, the N:P could be lowered at the head of the bay due to additional PO$_4^{3-}$ desorbing from riverine suspended solids or resuspended bottom sediment at the head of the bay stirred up as river discharge flowed past.
The relationship between N:P and distance from the head of the bay. The linear regression was fitted with a solid line when it represented a significant relationship (p-value < 0.05) and a dashed line when it is not significant (p-value > 0.05). The linear regressions fit to the N:P data from autumn (R² = 0.83), spring low tide (R² = 0.49), spring high tide (R² = 0.78), and summer (R² = 0.75) did not include the first data point. The first data point in summer is 20.09, and above the y-axis limits for the graph so not displayed.

As a particle reactive species, over 90% of the total PO₄³⁻ discharged by rivers is associated with suspended solids (Froelich, 1988). Desorption occurs in seawater because (1) surface seawater has low [PO₄³⁻] compared to rivers, and (2) anions competing for surface binding sites on suspended solids with PO₄³⁻ are all orders of magnitude greater in seawater than freshwater (Froelich, 1988). From our river ²²⁴Ra desorption experiment, the ratio of ²²⁴Ra adsorbed to fluvial suspended solids to dissolved ²²⁴Ra was 15:1 (Fig. 3.2) showing the potential increase of desorbing elements from suspended solids. Similarly, Froelich (1988) described 2- to 5-fold more PO₄³⁻ desorbed from riverine suspended solids than was dissolved in river water, making the desorbable fraction of PO₄³⁻ from riverine suspended solids a large input into coastal waters. Briefly, while river discharge was smaller than SGD and offshore mixing by two to three orders of magnitude (Table 3.2), it might still be an important source of PO₄³⁻ depending on sediment loads.
3.4.3.3 Silicic acid

As a dominant source of Si(OH)$_4$, SGD can influence the phytoplankton community. In both spring and summer, SGD was a greater source of Si(OH)$_4$ than river discharge or offshore mixing (Table 3.2). Indeed, consistent linear declines in seawater [Si(OH)$_4$] with distance from the mudflats ($R^2 = 0.89$ in spring at low tide, and $R^2 = 0.87$ in summer) implied a source at the bay’s head. SGD was also found to be an important source of Si(OH)$_4$ in nearby Kasitsna Bay (Lecher et al., 2016a) with incubation studies showing that the Si(OH)$_4$ discharged through SGD can promote the growth of diatoms (Lecher et al. 2017). In the NGA, common diatoms *Pseudo-nitzschia*, *Chaetoceros* and *Leptocylindrus* are dominant contributors to the spring and summer phytoplankton communities (Lecher et al., 2017; Tamburello et al., 2005). Lecher et al. (2017) suggested that in this region, *Pseudo-nitzschia* is favoured to dominate in areas of high SGD, whereas rivers promote the growth of *Chaetoceros* and *Leptocylindrus*.

3.5 Conclusions

SGD is an important contributor of macronutrients to nearshore coastal habitats in coastal Alaska. Findings from this paper suggested greater SGD in Alaska than the global average, largely driven by tidal pumping. The differing results from Ra- and Rn-based SGD estimates highlight the need to use various methods when quantifying this flux; however, the large Ra budget in glacial rivers laden with suspended solids may confound the Ra GW signal in many bays along the NGA coastline.

Our results showed that each of the major macronutrients (N, P, and Si) may have different input mechanisms into semi-enclosed bays in southcentral Alaska. NO$_3^-$ was the limiting nutrient in coastal seawater, and its input was dominated by offshore mixing and SGD in
spring (70 % and 30 %, respectively) and summer (40 % and 60 %, respectively), with no significant contribution from river discharge. Furthermore, SGD was a sink for PO$_4^{3-}$, which is introduced into the bay through mixing with more concentrated offshore water. But SGD was the dominant source of Si(OH)$_4$ to the nearshore environment (70 % in spring and 92 % in summer). Indeed, SGD is a major source of macronutrients to semi-enclosed bays in the NGA and should be considered as a critical component of marine biogeochemical cycles.
3.6 References


Barberio, M. D., Gori, F., Barbieri, M., Billi, A., Devoti, R., Doglioni, C., ... & Rusi, S. (2018). Diurnal and semidiurnal cyclicity of radon (222rn) in groundwater, Giardino spring, central Apennines, Italy. Water, 10(9), 1276.


Chapter 4 General Conclusion

The purpose of this research was to determine the role of submarine groundwater discharge (SGD) employing various measurement techniques. The comparison of SGD estimates from different methods is critical for this field where standard practice in field sampling and calculations is still actively being debated (Garcia-Orellana et al., 2021) and a unified approach remains elusive. Though SGD is absent in many coastal models, the findings of this thesis prove the importance of its inclusion. This highlights the importance of standard practice in SGD measurement.

4.1 Methodological Improvements and Novel Approaches

One significant achievement of this work confirmed that the method for estimating offshore $^{222}\text{Rn}$ mixing through the $^{222}\text{Rn}$ mass balance from Burnett and Dulaiova (2003) is valid. The peer-reviewed publication highlighting this work has been cited 606 times (number taken on 5/25/2022). To get to an SGD estimate, consecutive measurements of $^{222}\text{Rn}$ in the water column are subtracted from one another to get the flux of $^{222}\text{Rn}$ to seawater over that time increment. Since the $[^{222}\text{Rn}]$ decreases during flood tide (Fig. 3.5), these $^{222}\text{Rn}$ fluxes are negative. Burnett and Dulaiova (2003) hypothesize that by assuming strong mixing in the system, the greatest negative net $^{222}\text{Rn}$ flux is the offshore mixing term. Therefore, the absolute value of that number is added to every term. This method has recently been questioned by the field; however, the mixing loss term calculated in this study (91.1 Bq m$^{-2}$ hr$^{-1}$) is remarkably similar to the offshore mixing term calculated using the water residence time estimated with a tidal prism (91.3 Bq m$^{-2}$ hr$^{-1}$). These results support the hypothesis Burnett and Dulaiova (2003) put forth in their estimation of SGD.
Furthermore, this study adapted the method of calculating total SGD from $^{222}$Rn to calculate fresh SGD using a salt mass balance. Due to the dock in Jakolof Bay – our study site – being too far from the head of the bay to catch the tidal $^{222}$Rn signal and the presence of large macroalgae frequently clogging the pump attached to the radon detector, the timeseries of $^{222}$Rn was taken from a zodiac over 12 hours. A benefit of being on the water for the duration of the deployment permitted us to take hourly CTD profiles, which wouldn’t have been possible using an unsupervised mooring. We captured a signal of brackish SGD above the sediment at low tide (Fig. 3.7). Removing the top 1 m of the water column ensured that any river signal was excluded, and the subsequent mass balance was constructed using the same method as Burnett and Dulaiova (2003). This allowed for a direct comparison between the total and fresh SGD at the same location, the former calculated using $^{222}$Rn and the latter calculated using water column salinity.

4.2 Major Findings

This thesis addresses several gaps in our current understanding of SGD in sub-polar coastal environments. The previous SGD study undertaken at a rocky beach in the Northern Gulf of Alaska (NGA) estimated that SGD was one to two orders of magnitude greater than the coastal average (Dimova et al., 2015; Santos et al., 2021), likely due to the large tidal range (up to 8m) that drives the recirculation of seawater through sediment. Lecher et al. (2016) concluded that – assuming the SGD was similar across the entire NGA – more nutrients were delivered through SGD than river discharge in this region. This study confirmed that the SGD in a mudflat composed primarily of unconsolidated fluvial and glacial deposits (Bradley et al., 1999) had a similar flux rate as the rocky beach in the NGA, though these two sites are within 5 km of one
another. However, our study may not reflect the rate of SGD across the entire NGA since our fieldwork was conducted only during neap tide, and tidal amplitude is variable across the NGA, from $< 1$ m to 4 m (Fig. 4.1), so further studies in areas with a smaller tidal amplitude and during spring tide are required to estimate the full contribution of this region to global SGD.

![Figure 4.1 Tidal amplitude across the Northern Gulf of Alaska. This figure is taken from Kowalik (2004). The shading is the tidal amplitude of the sea level (in m) associated with the tide. The phase lines shows where any amplitude, usually a high and low, occurs simultaneously.](image)

The Ra adsorbed to the suspended solids in rivers make Ra-based SGD estimates difficult in glacier-dominated system. Jakolof Bay is part of a larger bay, Kachemak Bay, a hydrological system that is dominated by glaciated rivers. One of these rivers, Grewingk River, demonstrated the desorption of Ra from glacial flour was linear until a salinity of 15, before total desorption occurred, and no further Ra desorbed from the SS. Further research may elucidate whether this riverine Ra-signal masks the signal originating from groundwater.

While total SGD-derived nutrients are greater than the river discharge in many local environments around the world (Crotwell and Moore, 2003; Krest et al., 2000; Kim et al., 2003; Niencheski et al., 2007; Taniguchi et al., 2008; Burnett et al., 2007; Rodellas et al., 2015; Zhang
et al., 2020) – and on a global scale (Kwon et al., 2014) – it cannot be assumed to be the greatest source of all macronutrients. In Jakolof Bay, SGD was a source of Si(OH)₄ year-round, and seasonally a source of NO₃⁻. However, it was a sink of PO₄³⁻ and instead the element’s sources were offshore mixing and possibly desorption from fluvial suspended solids. Indeed, while having a river discharge an order of magnitude smaller than SGD, the river may still provide required nutrients to the nearshore environment for fueling primary production.

4.3 Future Directions

Due to the limitations associated with the temporary wells used in this study, future work would benefit from setting up permanent nested piezometers that can sample the aquifer at various depths. This approach is common for sites where there is more infrastructure and support for SGD research (Dulai et al., 2021). The PVC wells in this study were only able to reach 0.5 m below the surface of the sediment which accessed saline and fresh groundwater over the course of a tidal cycle (Fig. 3.3), but sampling for nutrients and ²²²Rn/Ra with depth and over tidal and seasonal cycles allow for a thorough understanding of groundwater endmembers and nutrient dynamics in the aquifer.

The nutrients from Jakolof River associated with suspended solids should be more fully characterized. Our study indicated that the fluvial suspended solids may contain adsorbed phosphate that releases into seawater as the river discharges into the estuary. A desorption experiment of phosphate from these suspended solids may support the hypothesis that rivers are a primary source of that macronutrient, even though the total river discharge is at least two orders of magnitude lower than SGD. Quantifying the dominant sources and sinks of
macronutrients into Jakolof Bay is critical in anticipating future changes to coastal food webs as primary production communities shift in response to nutrient availability.
4.4 References


