Geochemical Tracers Linking Submarine Groundwater Discharge to Hypoxia Formation in Long Bay, South Carolina, USA

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GEOCHEMICAL TRACERS LINKING SUBMARINE GROUNDWATER DISCHARGE TO HYPOXIA FORMATION IN LONG BAY, SOUTH CAROLINA, USA

by

Sarah Lynn Chappel

Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science in Coastal Marine and Wetland Studies in the College of Science Coastal Carolina University 2013

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Sarah L. Chappel

ABSTRACT

Long Bay, South Carolina has experienced hypoxic conditions (<2mg/L dissolved oxygen) in the nearshore environment, not fully attributed to traditional formation mechanisms. Past research suggested physical, biological, and/or anthropogenic influences on low dissolved oxygen levels. This project aimed to determine the contribution of submarine groundwater discharge (SGD) to hypoxia formation. We measured activities of $^{222}\text{Rn}_{xs}$, $^{224}\text{Ra}_{xs}$, $^{223}\text{Ra}$, $^{228}\text{Ra}$, and $^{226}\text{Ra}$ (3.8d, 3.6d, 11.5d, 5.8yr, 1600yr half-lives, respectively) in nearshore bottom waters from April 2012 through April 2013. Radium activities observed during a hypoxic event on 16-Aug-2012 were up to an order of magnitude higher than those seen during oxic conditions and the highest ever observed in the open ocean, to our knowledge. We determined that a hypoxic water mass, comprised heavily of offshore anoxic SGD, migrated inshore due to physical conditions constraining mixing over a two week time period. High groundwater content suggests that observed hypoxic conditions in nearshore Long Bay may be independent of biological influence once offshore SGD occurs.
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INTRODUCTION

Hypoxia is a phenomenon where the dissolved oxygen (DO) concentration in water decreases below 2 mg/L or 2ppm (Diaz and Rosenberg, 1995). At this level, low dissolved oxygen concentrations begin to stress living aquatic organisms. Although hypoxia occurs naturally in numerous coastal environments, such as bottom waters of fjords and marginal seas, recent occurrences in shallow nearshore and estuarine environments are linked to human influence rather than natural phenomena (Diaz and Rosenberg, 2008).

Several mechanisms can explain the formation of most hypoxic occurrences. Each mechanism requires some form of eutrophication – an increase in the rate of production and accumulation of carbon in aquatic systems resulting from excess nutrient loading (Nixon, 1995). As a result of increased nutrient availability, phytoplankton production increases, much of which sinks into bottom waters and is decomposed by aerobic bacteria, depleting oxygen concentrations (Rabalais et al., 2002). Most hypoxic conditions are found in bottom waters as this separation from the air-water interface inhibits re-equilibrium with atmospheric oxygen.

Input of excess nutrients from a major river or estuary can lead to eutrophication of a system. An example of this type of hypoxia formation occurs in the Gulf of Mexico due to increased nutrient loading from the Mississippi River. Hypoxia can also occur in coastal upwelling zones on the Western boundary of continental land masses, such as the Pacific Northwest, where upwelling brings deep nutrient-rich hypoxic water closer to the surface and into areas where organisms are not adapted to low levels of DO. Other areas, such as the Chesapeake Bay, are vulnerable to hypoxia because weather conditions can
greatly increase water column stratification. This stratification magnifies the effect of microbial growth and aerobic respiration in bottom waters, further increasing oxygen demand. Some areas, such as fjords, experience hypoxic or anoxic conditions because they are highly stratified due to limited mixing with other bodies of water (Diaz and Rosenberg, 2008).

Long Bay, which extends approximately 150km from Cape Fear, North Carolina to Winyah Bay, South Carolina (Figure 1), has experienced seasonal (June-September) hypoxic events documented over the last several years in the shallow nearshore (Libes and Kindelberger, 2010; Sanger et al., 2010). Long Bay, however, has few major riverine or estuarine inputs, undergoes open exchange with the ocean, and is not likely to experience substantial deepwater upwelling because it is located on a wide, shallow continental shelf. This location makes it likely that an upwelled water mass would undergo substantial biogeochemical changes during transit time to the nearshore environment, such as low dissolved oxygen events occurring in coastal regions of New Jersey (Glenn et al., 2004). Limited data suggest low dissolved oxygen is confined to the immediate nearshore, extending from Cherry Grove in northern Long Bay to Surfside beach in southern Long Bay (Libes, unpubl. data). Given that Long Bay does not directly fit with the known hypoxia mechanisms described by Diaz and Rosenberg (2008), an alternative mechanism must be invoked to explain the recently observed hypoxic events.

Preliminary evidence suggests that submarine groundwater discharge (SGD) could play a role in hypoxia formation in Long Bay, SC (McCoy et al., 2011). According to Moore et al., (2010), submarine groundwater discharge is “any and all flow of water on continental margins from the seabed to the coastal ocean, with scale lengths of meters to
kilometers, regardless of fluid composition or driving force.” Given the ubiquitous
nature of SGD, various components of coastal ecosystems can be affected by SGD.
Submarine groundwater discharge may have physical, chemical, and biological
influences on the environment that directly and indirectly affect the marine and terrestrial
ecosystem.

Exchange between coastal aquifers and seawater can impact the balance of
chemical budgets and coastal hydrologic systems. Groundwater is an important source of
freshwater in certain coastal waters, so its role in delivering excess nutrients is of
growing concern because of prevalent nutrient contamination of shallow groundwater
(USGS, 1999). Discharge of groundwater not only delivers terrestrially-derived macro-
and micro-nutrients to the coastal ocean, but can also mobilize nutrient products from the
diagenetic breakdown of organic matter in marine sediments (Froelich et al., 1979).
Nutrient concentrations and relative nitrogen:phosphorus ratios in groundwater are often
higher than surface waters (Hwang et al., 2005; Simmons, 1992; Moore, 1996; Krest et
al., 2000), which can further enhance biological growth in receiving waters and aid in the
development of eutrophication (Valiela et al., 1990).

Although SGD is often an overlooked source of nutrients in many areas, several
studies show SGD to play a critical role in nutrient addition and eutrophication. Valiela
et al. (1990) found that increased nutrient loads in groundwater entering several New
England bays led to higher levels of eutrophication, resulting in finfish and shellfish kills.
Great South Bay in New York attributed 50% of its total nitrogen input to groundwater
sources, which were polluted by Long Island septic systems (Capone and Slater, 1990).
Further, Simmons (1992) estimated that submarine groundwater discharge contributed
higher levels of phosphorus and nitrogen to coastal Georgia waters than river and stream discharge. Advective flows of SGD can also resuspend organic matter, making it available for bacteria to respire (Santos et al., 2012; Wainright and Hopkinson Jr., 1997). Therefore, even in cases where nutrient levels are not elevated in the terrestrial component of groundwater, the influx of SGD can still mobilize buried nutrients and carbon from shallow sediments.

The Grand Strand coastal region of Long Bay is heavily developed with resorts, residential, commercial, and industrial properties, as well as 102 year-round golf courses (Viso et al., 2010). Therefore, the anthropogenic influences of the region may strongly alter the nutrient characteristics of groundwater. Additionally, local groundwaters have other demonstrated characteristics that may aid in development of coastal ocean hypoxic conditions. Beach-face groundwater samples collected in Long Bay in 2012 were found to be devoid of dissolved oxygen (anoxic) (Peterson and Viso, unpubl. data).

Summertime temperatures of coastal groundwater have been documented in Long Bay as ~4°C cooler that surface water temperatures (Moore and Wilson, 2005; Peterson and Viso, unpubl. data), which could lead to increased stratification when substantial groundwater discharges into bottom waters occur. In order to determine how SGD may be affecting the chemical, physical, and biological processes in the coastal zone, researchers must determine the spatial and temporal dynamics of SGD and associated nutrient fluxes.

Santos et al. (2012) discuss different approaches to measuring submarine groundwater discharge. These are broadly classified as direct measurements, modeling techniques, and geochemical tracers. Direct measurements are the most basic and
spatially limited approach. Modeling techniques present the opposite problem in that they are extremely complex and involved, and usually focus only on the freshwater component of SGD (Charette et al., 2007), although recent work has begun to account for recirculating seawater (Li et al., 2009; Wilson, 2005). Using geochemical tracers to measure SGD is the most effective way to quantify physical interactions between groundwater and surface waters over local to regional scales. Ideal tracers are concentrated in groundwater relative to surface waters (usually 2-3 orders of magnitude) and remain relatively non-reactive in saline waters, allowing identification and measurement of the exchange between fresh and salt water (Moore, 1999). Radon and radium isotopes have been shown to be effective well-established geochemical tracers of SGD [see reviews by Burnett et al. (2006); Swarzenski (2007); Charette et al. (2008)] (Table 1).

Four naturally-occurring radium isotopes ($^{226}\text{Ra}$, $^{228}\text{Ra}$, $^{223}\text{Ra}$, and $^{224}\text{Ra}$) have a wide range of half-lives (1600yr, 5.8yr, 11.5d, and 3.6d, respectively) spanning the temporal scale of SGD processes. Radium becomes less particle reactive with increased salinity; therefore, radium desorbs from aquifer solids through cation-exchange, enriching saline SGD with excess Ra isotopes (Swarzenski et al., 2007; Mulligan and Charette, 2006; Krishnaswami et al., 1982). Once desorbed from particles, radium is chemically non-reactive, and therefore its concentration after discharge is generally only affected by decay and mixing (Swarzenski et al., 2007). Due to these behaviors, Ra isotopes are thought to only trace the saline component of submarine groundwater discharge. Estimates using mathematical modeling exercises suggest SGD along the
South Atlantic Bight (including Long Bay) is comprised of 96% recirculated seawater (Younger, 1996; Back et al., 1988).

Radon-222 is a naturally-occurring radioactive gas (half-life: 3.8 days) and has elevated concentrations in groundwater compared to ocean water (Burnett and Dulaiova, 2003). As a noble gas, \(^{222}\text{Rn}\) is conservative in nature (Cable et al., 1996) and concentrations are only reduced by decay, mixing, and atmospheric losses. Alpha recoil energies resulting from decay of the parent isotope, \(^{226}\text{Ra}\), on aquifer solids controls the production and input of \(^{222}\text{Rn}\) to groundwater (Fleischer, 1983).

In recent years, researchers in Long Bay have measured increased concentrations of \(^{222}\text{Rn}\) in bottom waters during hypoxic events relative to oxic conditions, as well as an inverse correlation between radon concentrations and DO levels (McCoy et al., 2011). From these correlations, McCoy et al. (2011) proposed a mechanism for the formation of a hypoxic water mass in Long Bay: that upwelling-favorable winds lead to limited cross-shelf mixing of nearshore waters, where inputs of SGD and terrestrially-derived nutrients concentrate in the warm, nearshore water. This suspected concentrating of nutrients is thought to increase heterotrophic activity and lower DO. However, using a single tracer in an often incompletely mixed water column, these authors were unable to definitively assess whether the increased radon concentrations are indicative of increased SGD (higher input rate) or decreased mixing (lower output rate). An additional tracer is needed to determine if the hypoxic water mass is associated with an increased SGD rate or limited dispersive mixing. Our objective was to use radium isotopes as an additional tracer to help delineate the behavior of groundwater in association with concurrent dissolved oxygen dynamics in Long Bay and to therefore better understand hypoxia.
development mechanisms. Prior to using radium isotopes to quantify SGD as it pertains to hypoxia in Long Bay, we first assessed the variability both spatially and temporally of radium isotopes in this system to offer broader context for hypoxia event-based observations.

METHODS

Spatial

Apache Pier, located in central Long Bay, South Carolina (33°45′41”N, 78°46′47” W; Figure 1) has been the focal point of Long Bay hypoxia research to date. The pier is the longest wooden pier on the East Coast, stretching approximately 200m into the nearshore environment (Apache Family Campground and Pier website). Apache Pier was the chosen research site because of the availability of a long-term continuous record of dissolved oxygen, temperature, and salinity (approximately 6 years), real-time water quality and meteorological data, and continuous in-situ radon activity measurements collected at the seaward end of the pier in 5-7m of water. We measured and quantified the concentration of radon and radium isotopes in bottom water from six locations along the pier (Figure 2) and several time-series events at the end of the pier to determine if the hypoxia process proposed by McCoy et al. (2011) is supported by radon and radium isotope observations.

Our six sampling stations were distributed along the length of Apache Pier and sampled weekly before and during the summer hypoxia season (April – September 2012) and monthly thereafter until April 2013. At each station, multiple bottom water samples (approximately 0.5m above the seabed) were collected and analyzed for various
parameters; including radium and radon activities, turbidity, temperature, specific conductivity/salinity, dissolved oxygen concentration, and oxygen saturation. We collected six liters of water with a peristaltic pump into air-tight bottles to determine radon activities (Stringer and Burnett, 2004). Sixty-liter samples were collected for radium isotope analysis. Turbidity of bottom water was measured onsite using a Hach 2100Q portable turbidimeter. Immediately after sampling, the following physical water column parameters were recorded at one meter vertical intervals at each station using a YSI multi-probe: temperature (°C), salinity (PSU; ‰), specific conductance (ms/cm), conductivity (S/m), dissolved oxygen concentration (mg/L), and oxygen saturation (%).

The six-liter air-tight samples were analyzed immediately upon return to the lab using a Rad-7 and protocol provided by Lee and Kim (2006) to determine radon concentrations. The sixty-liter radium samples were passed through chambers containing approximately 250mL of acrylic fibers impregnated with manganese dioxide (MnO₂) at a rate no faster than 1L/minute (Moore and Reid, 1973). The Mn fibers quantitatively extracted dissolved radium isotopes from the water samples. The Mn fibers were then analyzed by a Radium Delayed Coincidence Counter following procedures outlined by Moore and Arnold (1996) for ²²⁴Ra and ²²³Ra, as well as those from Peterson et al. (2009) for ²²⁶Ra. Select samples were analyzed via gamma spectrometry as outlined by Moore (1984) for ²²⁸Ra at the University of South Carolina. We report ²²⁴Ra and ²²²Rn concentrations as excess (i.e. ²²⁴Ra_ss and ²²²Rn_ss) because the parent isotopes are present in the system and therefore, must be corrected for what activity is supported.
**Temporal**

These weekly/monthly sampling events were designed to assess the offshore (spatial) variability of our tracers over seasonal time scales. In order to determine the variability over short (hourly) time scales, we conducted five time-series sampling campaigns in 2012 wherein we sampled hourly or semi-hourly for radium isotopes and physical parameters from Station 6 (adjacent to the continuous radon monitoring station) on 17-May, 19-Jul, 4-Aug, 14-Aug, and during a low dissolved oxygen event on 16-Aug. Vertical water column properties were also measured along the length of the pier and at Station 6 throughout each time-series event. Radon activities and other physical parameters from the pier monitoring station were coupled with sampling data to produce a complete data set. Radon and radium samples were also collected at 1m vertical intervals from 0.5m off the seafloor toward the surface to determine the variability of isotope concentrations during hypoxic and oxic conditions.

The continuous radon monitoring station provided temporal data to supplement spatial data obtained from weekly along-pier samples. The sampling from each of the six stations provided a spatial understanding of where SGD may be occurring from onshore to the end of the pier. The spatial component proved important because sampling during the 2011 and 2012 hypoxia season revealed hypoxic conditions at some, but not all stations along the pier. Due to this variability, a single continuous station may not fully account for the movement or location of maximal hypoxia as observable from the pier. Linking data sets from the spatial and temporal dynamics provided a more comprehensive picture of the system.
Endmembers

Beachface groundwater endmember samples were collected on 11-Jul-2012 from three piezometers at approximately 1m depth below land surface. Piezometers were manually installed during low tide at the approximate low-tide water line, mid-tide water line, and high-tide water line of the neap tide. We sampled each well hourly over a tidal cycle for radon and radium isotopes. Radon samples were collected using a peristaltic pump into 250mL air-tight bottles and analyzed on site using a Rad-7 following the WAT-250 protocol (Durridge Co., Inc.). Six-liter samples were also collected with a peristaltic pump and analyzed for radium isotopes upon return to the lab following the same protocol as used for the weekly radium sampling.

Three deep wells (~120m) from the maintenance irrigation system in a nearby subdivision (Arcadian Dunes; 33°45'56" N, 78°47'17" W) were sampled on 8-Nov-2012 for radon and radium endmember activities. The irrigation hoses filled a 5L bucket and continued to overflow the bucket to minimize degassing while a peristaltic pump collected discrete samples into 250mL air-tight bottles. All samples were analyzed following the same protocol as used for the July 2012 endmember sampling event.

To obtain representative endmembers from the fully submerged sediments, two established wells (~3.3m deep) were sampled on 8-Nov-2012. Each well was sampled using a suction pump that fed water into an overflowing 5L bucket. Samples for radium (60L sample) and radon (6L sample) were extracted from the bucket using a peristaltic pump and measured in the lab following the analytical protocols outlined above.
RESULTS AND DISCUSSION

Overview

In this manuscript, we present and discuss the chemical and physical parameters of each sampling station on the pier to determine the spatial variability of the nearshore system (Table 2). We then examine the temporal variability of radium isotopes and physical properties using data from five time-series sampling events. We present what we consider “normal” radium isotope activities in the nearshore. We further investigate activities during a low DO event, which we consider hypoxic conditions, on 16-Aug-2012. During this event, the local beachface endmembers cannot support the measured activities. We eliminate other potential sources of radium to the system and then consider an offshore groundwater source. Using this offshore groundwater source, we determine the residence time of bottom water samples collected prior to and during the hypoxic event to demonstrate a relatively consolidated (i.e., unmixed) groundwater discharge layer advecting inshore from carbonate aquifers which outcrop farther offshore. We investigate the contribution of anoxic groundwater to the dissolved oxygen concentration budget by determining the groundwater composition of oxic and hypoxic samples.

Spatial Variability

We chose six sampling stations along the pier 0, 49, 90, 140, 179, and 198 meters offshore (Stations 1-6, respectively; Figure 2) to delineate the spatial variability of radium isotopes and physical parameters of the nearshore system. Station 1 was positioned at the approximate neap mid-tide line and serves as the distance benchmark from which the other stations are measured.
We sampled Station 1 (0m from the mid-tide water line) when the tides permitted. Bottom water sampling required almost a meter of water to effectively sample without clogging pumps and tubing with sediment. We were able to sample Station 1 on ten sampling events, during which water depths ranged from 0.90-2.74m. Average dissolved oxygen concentration at this station was 7.48±0.82mg/L (Figure 3), which was higher than other station averages, likely due to Station 1 experiencing higher wave action. Radium isotope activities were quite variable across the 10 sampling events. Station averages were as follows: 0.019±0.017dpm/L ($^{223}$Ra), 0.140±0.083dpm/L ($^{224}$Ra$_{ss}$), and 0.129±0.097dpm/L ($^{226}$Ra) (Figure 4). Excess $^{222}$Rn activities varied even more than radium isotope activities at Station 1, ranging from 0.0-13.390dpm/L (Figure 5). Average $^{222}$Rn$_{ss}$ activity at Station 1 was 2.296±3.991dpm/L, similar to other stations along the pier (Figure 4).

Stations 2 and 3 (49m and 90m offshore, respectively) had similar averages for all parameters during oxic conditions (Figure 3), likely due to similar depth ranges throughout the season (Station 2: 1.08-3.58m; Station 3: 2.15-4.26m; n=24). Radium isotope activities were also similar between Stations 2 and 3, with each station’s averages varying less than 8% for $^{223}$Ra, 12% for $^{224}$Ra$_{ss}$, and 6% for $^{226}$Ra (Figure 4). Average excess radon activity was more variable at Station 2 (2.434±3.030dpm/L) than Station 3 (2.057±1.647dpm/L) (Figure 4), but yielded similar activities on a weekly basis.

Station 4 (149m offshore) had an average depth of 5.13m during the sampling season with an average dissolved oxygen concentration of 6.67±1.17mg/L. The average $^{223}$Ra activity was 0.020±0.018dpm/L and the $^{226}$Ra average was 0.144±0.106dpm/L. Excess $^{224}$Ra varied less than the other two isotopes, with an average activity of
0.142±0.076dpm/L (Figure 4). Samples from Station 4 had frequent anomalously high radon concentrations compared to the other five stations (Figure 5). Average excess radon activity during oxic conditions at Station 4 was 6.866±8.021dpm/L with a range of 34.224dpm/L over the course of the sampling season – double the average activities at all other stations (n=24). Interestingly, the parent $^{226}$Ra activities at Station 4 were not significantly higher than other stations. This could suggest a higher fresh SGD input at Station 4 than other stations, as radium is thought to only trace saline groundwater. However, salinity measurements at Station 4 do not support this assumption, as they were similar to the other five stations. We speculate that one or several pier pilings at this site may have breached a confining layer and provided a conduit for local groundwater discharge.

Depth at Station 5 ranged from 5.81-8.01m throughout all sampling events, making this station the deepest of the six stations. At Station 5, the average observed dissolved oxygen concentration was 6.53±1.13mg/L and oxygen saturation was 91.8±9.9% (Figure 3). The lowest short-lived radium isotope average activities during oxic events of all the stations along the pier; $^{223}$Ra 0.017±0.013dpm/L and $^{224}$Ra $\alpha_x$ 0.131±0.061dpm/L (n=24), were also observed at this station (Figure 4). Radium-226 average activity (0.143±0.097dpm/L) was similar to Stations 1-4, and roughly eleven percent higher than the average activity at Station 6 (Figure 4).

Station 6, located the farthest offshore (approximately 198m from mid-tide water line) ranged in depth from 5.05-8.01m throughout the sampling season. Average dissolved oxygen concentration of bottom water at Station 6 during oxic weekly/monthly and time-series events was 6.09±0.86mg/L (n=67). Isotope activities during oxic
conditions were 0.025±0.015dpm/L for $^{223}\text{Ra}$, 0.177±0.057dpm/L for $^{224}\text{Ra}_{\text{xs}}$, and 0.176±0.103dpm/L for $^{226}\text{Ra}$ (n=67). Average $^{222}\text{Rn}_{\text{xs}}$ activities during oxic conditions were 3.108±2.290dpm/L, slightly higher than all other stations except Station 4, which had roughly twice the average $^{222}\text{Rn}_{\text{xs}}$ activity.

Weekly and monthly sampling efforts at each station revealed little spatial variability of physical parameters along the length of the pier within the resolution limits of the YSI sonde (uncertainty ±0.1°C, ±0.5PSU). Both temperature and salinity measurements showed low standard deviations from the mean for each individual weekly/monthly sampling event. Along the pier, bottom water temperature only varied ±0.51°C during any sampling event. Bottom water salinity deviated ±0.36‰ during the 3-Jul-2012 sampling, but varied ±0.19‰ or less during all other weekly sampling events. Dissolved oxygen levels varied slightly more along the length of the pier each week with standard deviations up to ±1.32mg/L (Figure 3). Inshore stations consistently showed higher levels of dissolved oxygen compared to the stations farther offshore. This pattern is likely due to the shallow nature of the inshore stations and that they are located in the surf zone where subsurface and surface wave turbulence enhances oxygenation of the water.

From April 2012 - April 2013, radium isotope activities during any single sampling event collected along the pier’s six stations during oxic conditions showed no significant spatial patterns (Figure 5). No significant correlation of radium activity with distance offshore was seen in any single oxic sampling event (p>0.05, n=5-6). Due to non-significant variability in radium isotope activities along the pier during each oxic sampling event (Table 3), we chose to use Station 6 (198m from shore) as a
representative station of the system for more in-depth temporal variability sampling. Not only is Station 6 the farthest offshore, it is also adjacent to the continuous monitoring station, adding value to its representative nature. Seasonal average isotope activities at Station 6 were slightly lower than the average along-pier activities (\(^{226}\text{Ra} : -0.011 \text{dpm/L}, \)\(^{224}\text{Ra}_{xs} : -0.0003 \text{dpm/L}, \)\(^{223}\text{Ra} : -0.001 \text{dpm/L}\)) making Station 6 a conservative representation. Lack of along-pier variability is not surprising, considering the stations are less than 200m apart and the differences in depth only vary up to 7.11m.

**Temporal Variability**

Isotope activities and physical parameters at Station 6 varied temporally throughout the season. Temperature varied substantially throughout the sampling season, as to be expected with warmer temperatures in the summer and autumn and cooler in the winter and spring. Subsequently, dissolved oxygen concentration and oxygen saturation were generally higher during colder sampling events, likely due to increased gas solubility and less heterotrophic biological activity to draw down the oxygen in colder water. Radium isotope activities were fairly homogenous throughout the year, aside from an increase at the end of July through the middle of August, which we explain later in this manuscript. Week to week variability of activities was relatively low, aside from an almost five-fold decrease in \(^{223}\text{Ra}\) and \(^{224}\text{Ra}_{xs}\) activities from 19-June to 26-June; however \(^{226}\text{Ra}\) only decreased by a factor of 1.7.

We hypothesized that changes in activities occurring on weekly, biweekly, or monthly time scales were related to water depth (i.e. tidal stage) or lunar phase (i.e. spring/neap tides). We set up five separate time-series sampling events in 2012 (17-May, 19-Jul, 4-Aug, 14-Aug, 16-Aug) to examine the temporal variability of activities on a
shorter time scale (<24hrs). No significant correlation was shown between radium isotope activities and sampling point in the tide (i.e. water depth) during oxic conditions at Station 6 (n=62; $^{223}$Ra $r=0.022$, $^{224}$Ra$_{ss}$ $r=0.062$, $^{226}$Ra $r=0.116$). We then examined the relationship of radium activities with lunar phases and determined there was no correlation with spring/neap tides. We concluded that the large excursions in the long-term data set (i.e. considerable increases in activities during late July to mid August) were not caused by the tidal stage present at the time of sampling.

Data from the five time-series events at Station 6 (Table 4) show inverse correlations between bottom water salinity and dissolved oxygen levels ($r=0.884$, n=57, p<0.001). Temperature and dissolved oxygen levels also show an inverse correlation when the 17-May event is discounted as an outlier (due to much cooler water temperatures as the following four time-series events ($r=0.940$, n=51, p<0.001). Data from the time-series events revealed $^{226}$Ra activities and oxygen saturation (%) are inversely correlated ($r=0.894$; n=57; p<0.001) (Figure 6). Short-lived radium isotopes are also inversely correlated with oxygen saturation; $^{224}$Ra$_{ss}$ ($r=0.787$; n=57; p<0.001) and $^{223}$Ra ($r=0.878$; n=57; p<0.001) (Figure 6). Consequently, a significant negative correlation exists between bottom water radium isotope activities and dissolved oxygen concentration: $^{226}$Ra, $r=0.894$; $^{224}$Ra$_{ss}$, $r=0.887$; $^{223}$Ra, $r=0.816$ (n=56; p<0.001); as well as between radium isotope activities and bottom water temperature (excluding the 17-May event as an outlier). The same five time-series events revealed bottom water $^{226}$Ra activities and salinity are positively correlated ($r=0.792$; n=56; p<0.001), as well as $^{223}$Ra and $^{224}$Ra$_{ss}$ activities with salinity ($r=0.801$ and $r=0.799$, respectively; n=56, p<0.001).
The continuous time-series monitoring station on the pier also revealed an inverse relationship between oxygen dynamics and radon activity throughout the summer.

The weekly/monthly sampling along the pier and the time-series events at Station 6 helped us to determine that there was no spatial variability along the length of the pier, nor temporal variability as a function of tidal influences. As a result of the lacking variability, we established radium isotope activities we consider “normal” (i.e. representative) for the inshore system and would expect to see throughout the season. These activities are 0.025dpm/L ($^{223}$Ra), 0.177dpm/L ($^{224}$Ra$_{ss}$), and 0.176dpm/L ($^{226}$Ra).

We used the representative radium isotope activities to further investigate the hypoxic event on 16-Aug-2012. During the nearshore hypoxic event, the bottom water dissolved oxygen dropped 1.48mg/L in approximately 5 hours and abruptly rose 2.32mg/L in 2 hours. The changes from 3.82mg/L at 08:50 to 2.34mg/L at 14:00 and subsequent rise to 4.66mg/L at 16:00 all occurred during ebb tide, one day before maximal spring tide. The rapid increase in dissolved oxygen from 14:00-16:00 is correlated with an increase in temperature (0.7$^\circ$C) and a decrease in salinity (0.5‰). The rapid fluctuations in dissolved oxygen levels and temperature led us to believe the driving force was strongly physical, rather than biological; similar to observations and water mass advection hypotheses by McCoy et al. (2011).

**Hypoxic Event**

To further explore the groundwater influence on the hypoxic event, we measured radium activities in the bottom water at Station 6 at 30 minute intervals throughout the event. All isotope activities varied throughout the hypoxic sampling event, but were significantly higher than average pier activities during oxic conditions (Figure 7). Ra-
228 activities (5.25±0.83dpm/L) were almost five times higher than $^{228}$Ra activities from the 14-Aug event (1.11±0.11dpm/L), only two days previous. Average $^{223}$Ra activities during the hypoxic event (0.161±0.027dpm/L) were more than six times greater than normal activities (0.025±0.015dpm/L). Excess $^{224}$Ra activities in the hypoxic samples showed a two-fold increase and $^{226}$Ra activities showed a ten-fold increase from average seasonal activities during the hypoxic event. Local and regional $^{226}$Ra activities have been measured several times before this project from nearshore and offshore (Moore et al., 2002; Moore and Wilson, 2005). However, activities during the 16-Aug-2012 hypoxic event at Apache Pier are the highest reported to date for Long Bay surface waters. In fact, to our knowledge, $^{226}$Ra activities approaching $\geq 2.2$dpm/L have never been observed in surface waters. Past research estimated the $^{226}$Ra activity of nearshore waters in Long Bay to be 0.151±0.040dpm/L (Moore, 1996) and typical open ocean concentrations of radium isotopes seaward of Long Bay to be 0.08dpm/L (Broecker, 1963); both at least an order of magnitude lower than activities measured during hypoxia. The continuous monitoring station also recorded an inverse relationship between dissolved oxygen saturation and radon activity throughout this hypoxic event (Figure 8; $r=0.701$, $n=407$, $p<0.001$).

A vertical water column profile of radium isotopes and physical parameters during the hypoxic event (17-Aug-2012) revealed obvious vertical stratification (Figure 9). Not only do all four measured radium isotopes have higher activity in the deepest samples, but there is also a temperature stratification of $1^\circ$C between the surface and bottom waters, furthering the argument that the driving force of hypoxia is associated
with cooler, higher activity groundwater. Salinity showed no stratification (as detectable with our equipment) with a 0.2‰ increase from surface to bottom waters.

Since bottom water activities of radon and radium isotopes were significantly higher during the hypoxic event, we faced the question as to whether higher activities are a result of increased SGD or decreased mixing. To begin to delineate this issue, we examined the local source of groundwater to the nearshore system.

**Local Endmember Analysis**

On 10-Jul-2012, we installed three wells in the intertidal zone near Apache Pier and sampled each well every 1.5 hours through a full tidal cycle. Beachface Well 3, located at the high tide water line, showed higher radium isotope activities than the other wells. This is likely due to the less frequent tidal pumping and wave action as these processes reduce the porewater activities by recirculating lower activity surface water into the unconfined aquifer (Santos et al., 2012). Radium-226 showed a significant negative correlation with tidal level throughout the sampling event ($r=0.630$, $n=27$, $p<0.001$). Higher activities were measured during lower water levels, likely due to less head pressure during low tide. We also sampled two wells managed by Apache Pier on 13-Nov-2012, to further investigate local endmembers. Both of these wells were approximately 3.3m below sand surface, one located at the low tide water line, and one between pier Stations 1 and 2. This additional sampling of endmembers did not reveal higher activities for any radium isotopes than were seen during the summertime beachface sampling. Sampling of beachface and surfzone radium isotope endmembers during this project represented the first attempt to do so in this region. Past research
(McCoy et al., 2011; Viso, unpubl. data) sampled beachface and surfzone porewaters along Long Bay for radon and nutrients, but no radium isotope activities were analyzed. Out of the three beachface wells and two pier-managed wells, only Beachface Well 3 showed one sample with a higher activity of $^{223}\text{Ra}$ than the highest sampled during hypoxia (only 0.003dpm/L higher). The lowest $^{223}\text{Ra}$ activity measured during hypoxia (0.120dpm/L) was still higher than the average beachface endmember activity (0.090dpm/L) (Figure 10). Average $^{224}\text{Ra}$ activities during hypoxia were lower than four of the five endmember well average activities, with Pier Well 2 (0.343dpm/L) being only slightly lower than the hypoxic average (0.359dpm/L). Radium-226 activities during hypoxia, however, were significantly higher than any sampled endmember activities. The highest observed $^{226}\text{Ra}$ activity during hypoxia was 2.246dpm/L – three times greater than the highest endmember sampled from the wells (Figure 10).

The significant difference in measured radium activities during oxic levels and the hypoxic event led us to believe samples taken during the hypoxic event were derived from a separate water mass, consistent with the proposed hypoxic water mass (HWM) by McCoy et al. (2011). Due to seasonal sampling efforts showing all surface and groundwater $^{226}\text{Ra}$ activities to be lower than the observed hypoxic activities, we concur that the HWM accumulated from a source different than the unconfined aquifer discharge. This assumption of an aging water mass is further promoted because the degree of enrichment of each radium isotope during the hypoxic event correlates to their respective half-lives.
Other Sources of Radium

Moore (1996) estimated SGD to account for approximately 40% of total riverine flow throughout the South Atlantic Bight; therefore, we must investigate the potential for radium enrichment to the nearshore waters from sources other than groundwater. Other potential sources of radium isotopes to the nearshore system include riverine and tidal creek inputs, stormwater runoff, and offshore waters transported to the nearshore.

Riverine sources to Long Bay include Winyah Bay, 70km south of Apache Pier, and Little River and Cape Fear River to the north. Using \(^{222}\text{Rn}\), McCoy et al. (2011) determined the discharge rates and required transit time for input from the three rivers would not produce the high activities observed during hypoxic events at Apache Pier. Moore (1996) measured the activity of \(^{226}\text{Ra}\) in surface waters on nearshore to offshore transects adjacent to Winyah Bay, Myrtle Beach, and Cape Fear. All of the observed activities were substantially lower (at least an order of magnitude) than those seen during hypoxia, thus eliminating riverine inputs as a source of radium enrichment during hypoxia.

Singleton Swash, a tidal creek located approximately 2.4km south of Apache Pier, has been shown to have high activities of \(^{222}\text{Rn}\) (Peterson et al., unpubl. data), implying that radium may also be enriched in the tidal creek. However, the main source of radon and radium to the tidal creek would be from groundwater since there is no terrestrial headwater source to the swash, and because the local groundwater does not have the radium activities required to support the hypoxic levels, we can disregard the tidal creek as a source of high radium enrichment during hypoxia.
The potential for offshore sources of radium, not supplied by groundwater, to support the hypoxic activities is also unlikely. Diffusion from sediments would not contribute to $^{226}\text{Ra}$ activities, as the long half-life renders diffusion processes negligible. Phosphate-rich deposits would not contribute to $^{228}\text{Ra}$ activities, as it is part of the thorium decay series. Moore (1996) determined the open ocean concentration of $^{226}\text{Ra}$ to be 0.08 dpm/L in the South Atlantic Bight – two orders of magnitude lower than activities seen during hypoxia. Eliminating these other potential sources of radium furthers our assumption that the only pathway for the high radium activities measured during hypoxia is offshore submarine groundwater discharge.

**Offshore Groundwater Sources**

Due to the low concentration of $^{223}\text{Ra}$ and $^{226}\text{Ra}$ (0.090 and 0.504 dpm/L, respectively) in local beachface groundwaters and their inability to support activities measured during hypoxia (0.161 and 1.634 dpm/L, respectively), we must consider an alternative source of SGD. Moore and Wilson (2005) and unpublished data from Moore present radium activities from ten offshore wells approximately 25 km east of Myrtle Beach, SC. The wells were set to limestone basement, often through a clay confining layer under sandy sediments. Moore and Wilson (2005) suggested the high porosity zone in some of the wells may be active karst surface. Each of the ten wells was sampled from their installation in 1999 through 2004 for $^{226}\text{Ra}$, $^{228}\text{Ra}$, $^{223}\text{Ra}$, $^{224}\text{Ra}$, and salinity. We examined the activity ratios of $^{228}\text{Ra}/^{226}\text{Ra}$ in each of the ten wells and our hypoxic samples (Figure 11). Of the ten wells, seven revealed high enough $^{226}\text{Ra}$ activities to support the activities observed on 16-Aug. Of those seven wells, only three wells (Wells A, R, and LW) had $^{228}\text{Ra}$ activities high enough to support the hypoxic samples (Figure
11). Each of these three wells was sampled and analyzed for all four radium isotopes, and subsequent activity ratios. Activity ratios (AR) of $^{228}\text{Ra}/^{226}\text{Ra}$ for 37 samples from Wells A, R, and LW showed significant positive correlation with the $^{228}\text{Ra}/^{226}\text{Ra}$ AR for the 16 hypoxic samples ($r=0.958$, $n=53$, $p<0.001$) (Figure 12). This relationship leads us to believe the hypoxic water mass we sampled on 16-Aug was heavily comprised of offshore SGD from groundwaters represented by samples from Wells A, R, and LW. The question then becomes: how did this water mass move 25km inshore without thoroughly mixing with lower activity surface water and how did it acquire its hypoxic characteristics?

Moore et al. (1998) highlights weather conditions during their 1994 study, noting that sustained southwest winds increased vertical stratification with an intrusion of deeper water, brought inshore by the upwelling-favorable winds. McCoy et al. (2011) noted a similar upwelling-favorable wind pattern in the weeks before their sampled hypoxic events in 2009. During 2012, winds were primarily out of the southwest from 16-June through 19-Aug, setting up a similar offshore front which limited open ocean mixing in Long Bay (Figure 13). This limited mixing mechanism, coupled with calculations of increasing ages of water with increasing distance from shore (Moore, 2000) and the aforementioned AR relationship with offshore groundwater, further supports our proposed HWM forming from offshore SGD and migrating inshore. Because we were not able to determine the SGD rates of the offshore sites, we then aimed to determine the age and groundwater composition of the water mass.
Activity ratios greatly vary between oxic samples and hypoxic samples. Activity ratios for $^{224}\text{Ra}_{xs}/^{223}\text{Ra}$, $^{224}\text{Ra}_{xs}/^{226}\text{Ra}$, and $^{223}\text{Ra}/^{226}\text{Ra}$ were all lower during the hypoxic event. The larger difference in ratios containing the short-lived $^{224}\text{Ra}_{xs}$ isotope gives us further evidence that the HWM aged as it moved inshore, causing significant decay of the shortest-lived isotope. With a 3.6 day half-life, $^{224}\text{Ra}$ will experience considerable decay after three weeks, leaving the remaining $^{224}\text{Ra}$ fully supported and $^{224}\text{Ra}_{xs} = 0$. Because we correct our measurements for $^{224}\text{Ra}$ supported by dissolved $^{232}\text{Th}$, any measured activity is considered excess and therefore assumed to be injected from an external source. The $^{224}\text{Ra}_{xs}$ activities we measured during hypoxia were twice our normal activities, which led us to believe the local beachface SGD may have contributed to the measured activity during hypoxia. Radon-222 and $^{224}\text{Ra}_{xs}$ (the short-lived isotopes of interest) are the only isotopes measured during hypoxia that the local beachface endmembers could chemically support. Radium-223 and $^{226}\text{Ra}$ hypoxic activities, and subsequent activity ratios, cannot be supported by the local beachface endmembers; therefore, we can use the offshore endmembers to calculate the age of the HWM.

The first step in calculating residence time of our samples is to determine the percent composition of groundwater using the long-lived $^{226}\text{Ra}$ isotope in each sample with the equation:

$$%_{gw} = \frac{226\text{Ra}_{gw} - 226\text{Ra}_{sw} (dpm/L)}{226\text{Ra}_{gw} - 226\text{Ra}_{sw} (dpm/L)} \times 100$$  \hspace{1cm} (1)$$

where $^{226}\text{Ra}_{sw}$ is a constant representing the average surface water concentration of $^{226}\text{Ra}$. We use the average $^{226}\text{Ra}$ bottom water activity (0.176dpm/L) throughout all oxic sampling events as a highly conservative estimate of surface waters, assuming the water
column was well mixed during each of the oxic sampling events. The $^{226}\text{Ra}_{gw}$ groundwater constant (5.275 dpm/L) is the average activity of $^{226}\text{Ra}$ in the three offshore wells (Well A, Well LW, and Well R) that provide the best activity ratio fit to our samples (Moore and Wilson, 2005; Moore, unpubl. data), and $^{226}\text{Ra}_{bw}$ is the activity of each bottom water sample (Table 5). We then determine the expected activity of $^{223}\text{Ra}$ in the water samples based on adjusting the endmember activity from these wells by the percent groundwater calculated by $^{226}\text{Ra}$:

$$223\text{Ra}_WM (dpm/L) = 223\text{Ra}_{gw} (dpm/L) \cdot \%_{gw}/100$$

(2)

Where $^{223}\text{Ra}_{gw}$ is the average activity of $^{223}\text{Ra}$ in the offshore wells (Moore, unpubl. data). We then solve for the basic decay equation for time:

$$T = \ln[223\text{Ra}_{bw} / 223\text{Ra}_WM (dpm/L)] / -\lambda$$

(3)

$$\lambda^{223}\text{Ra} = \ln(2) / T_{1/2}$$

(4)

Where $^{223}\text{Ra}_{bw}$ is the activity observed in the bottom water sample, $^{223}\text{Ra}_WM$ is the expected activity in the water mass from Eq. 8 and $\lambda$ is the decay constant of $^{223}\text{Ra}$ (0.060065).

Residence time calculations during oxic sampling events were 3.4±4.1, 5.5±3.7, and 10.9±4.0 days for 4-Aug (n=7), 7-Aug (n=6), and 14-Aug (n=5), respectively (Table 5). These average residence times have significant linear correlation $r=0.999$, n=3, $p<0.001$ (Figure 14). We also calculated the residence time as discussed above using $^{224}\text{Ra}_{xs}$, which yielded similar residence times of 4.8±1.5, 5.7±1.0, 8.4±1.4 days for 4-Aug, 7-Aug, and 14-Aug, respectively. These averages also reveal a significant linear correlation $r=0.998$, n=3, $p<0.001$ (Figure 15). Thus, we assume the water mass sampled
during those three events was the same water mass, remaining in the nearshore environment, decaying and not substantially mixing with lower activity water (Table 5).

The hypoxic event on 16-Aug averaged a residence time of 17.2±3.7 days when calculated using $^{223}$Ra activities and 14.0±1.2 days with $^{224}$Ra$_{ss}$ activities. These much higher residence times imply addition of older water to the system, rather than the same water mass sampled on 4-, 7-, and 14-Aug. Moore (2000) calculated the ages of surface waters using radium isotope activity ratios along offshore transects from Myrtle Beach as well as transects north and south of Myrtle Beach. In the Myrtle Beach transect, samples were younger than transects to the north (Cape Fear) and south (Winyah Bay). Ages were less than 15 days within 25km offshore for both the Cape Fear and Winyah Bay transect, whereas the Myrtle Beach transect did not yield ages above 15 days within 80m of the shoreline. This further supports an offshore source of our high activity, hypoxic samples.

**Groundwater and Oxygen Dynamics**

Now that we determined the percentage of groundwater during each sampling event, we can explore the potential effects of the groundwater on the dissolved oxygen levels in the water mass. High sulfide concentrations in offshore well groundwater samples (Moore, unpubl. data) indicates these source waters are anoxic (0.0mg/L). Using the “normal” dissolved oxygen concentration (6.09mg/L) for the system, we then factor in the percentage of groundwater for each sample at 0.0mg/L to estimate DO concentrations based on mixing calculations presented above. The calculated DO levels are similar to the average concentrations observed during the sampling events (Figure 16, Table 5). In this case, SGD alone can account for the observed depletion of dissolved
oxygen in the sampled water mass. These calculations suggest that the oxygen budget may not require additional biological drawdown (net respiration) once submarine groundwater discharge takes place for the inshore system to experience oxygen levels low enough to stress aquatic life.

CONCLUSIONS AND RECOMMENDATIONS

Long Bay, South Carolina experiences hypoxic and low dissolved oxygen events spanning hours to days that are unattributable to the typical formation mechanisms outlined by Diaz and Rosenberg (2008). Preliminary evidence showed increased concentrations of $^{222}$Rn in bottom waters during low DO events and an inverse correlation between radon concentrations and DO levels, which suggests that SGD could play a critical role in hypoxia formation. McCoy et al. (2011) proposed a mechanism that wind patterns lead to limited cross-shelf mixing of warm, nearshore waters where inputs of SGD and terrestrially derived nutrients concentrate, increasing heterotrophic activity (Smith et al., 2010) and lowering DO. These authors were not able to definitively determine whether the increased radon concentrations are indicative of increased SGD or decreased mixing. We hypothesized that radium isotopes would serve as additional tracers to delineate the effects of higher input rate versus lower output rate on observed radon concentrations and better understand the spatial and temporal variability of radium and DO dynamics, as well as development mechanisms of a hypoxic water mass. Seasonal and time-series sampling of bottom waters during oxic and hypoxic conditions provided us with a comprehensive understanding of the inshore system. However, radium isotope activities during the 16-Aug-2012 hypoxic event could not be supported by the local beachface endmembers. We identified offshore groundwater sources (Moore
and Wilson, 2005; Moore, unpubl. data) with similar activity ratios of $^{228}\text{Ra}/^{226}\text{Ra}$ as our hypoxic samples. We calculated residence times using the offshore groundwater as endmembers and concluded that samples taken from 4-Aug through 14-Aug were of the same water mass, decaying in the nearshore and not mixing with lower activity water over a 10 day period. We also concluded that samples taken during the hypoxic event were of a different water mass than sampled in the previous weeks; minimum residence time calculations determined the hypoxic water mass was at least two weeks old. The significant differences in radium isotope activities during oxic and hypoxic conditions and the dissimilarity in calculated residence times suggest that a hypoxic water mass comprised largely of groundwater migrated inshore under the influence of certain physical conditions. After calculating the percentage of anoxic groundwater in each sampled water mass, we propose that hypoxic levels of dissolved oxygen in Long Bay may be independent of biological demand once offshore SGD occurs.

Future research should to be undertaken to identify if submarine groundwater discharge from the offshore wells is occurring under specific physical conditions, or is constantly occurring but normally mixing with lower activity waters. Once SGD drivers have been identified, we recommend further investigation into the physical conditions required to move the hypoxic water mass inshore, relatively undisturbed. Determining the extent of the hypoxic water mass in Long Bay will also add insight to movement capability. Not only do hypoxic conditions negatively affect aquatic life, but also can impact the local Grand Strand economy, thus adding increased importance to further investigation of hypoxia phenomena in Long Bay, South Carolina.
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evidence of water exchange through a coastal aquifer: Implications for nutrient


TABLES

Table 1. Radon and radium isotope half-lives and properties.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Half Life</th>
<th>Property</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ra-224</td>
<td>3.6 days</td>
<td>Solid</td>
</tr>
<tr>
<td>Ra-223</td>
<td>11.5 days</td>
<td>Solid</td>
</tr>
<tr>
<td>Ra-228</td>
<td>5.8 years</td>
<td>Solid</td>
</tr>
<tr>
<td>Ra-226</td>
<td>1600 years</td>
<td>Solid</td>
</tr>
<tr>
<td>Rn-222</td>
<td>3.8 days</td>
<td>Gas</td>
</tr>
</tbody>
</table>

Table 2. Apache Pier established sampling station information. Average and standard deviation from the mean for each station during oxic conditions. Distance offshore from neap mid-tide water line. N = number of bottom water radium samples taken at each station from April 2012 – April 2013.

<table>
<thead>
<tr>
<th>Sta.</th>
<th>Distance (m)</th>
<th>Depth (m)</th>
<th>N</th>
<th>DO (mg/L)</th>
<th>Saturation (%)</th>
<th>Salinity (%)</th>
<th>Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0.90-2.74</td>
<td>10</td>
<td>7.48±0.82</td>
<td>103.10±1.02</td>
<td>34.4±0.7</td>
<td>21.6±6.0</td>
</tr>
<tr>
<td>2</td>
<td>49</td>
<td>1.08-3.58</td>
<td>24</td>
<td>7.21±0.83</td>
<td>101.51±3.10</td>
<td>34.4±0.7</td>
<td>22.8±5.6</td>
</tr>
<tr>
<td>3</td>
<td>90</td>
<td>2.15-4.26</td>
<td>24</td>
<td>7.01±1.01</td>
<td>98.78±6.71</td>
<td>34.3±0.7</td>
<td>23.0±5.7</td>
</tr>
<tr>
<td>4</td>
<td>140</td>
<td>3.92-6.05</td>
<td>24</td>
<td>6.67±1.17</td>
<td>93.56±9.75</td>
<td>34.3±0.7</td>
<td>22.8±5.7</td>
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<tr>
<td>5</td>
<td>179</td>
<td>5.81-8.01</td>
<td>25</td>
<td>6.53±1.13</td>
<td>91.80±9.88</td>
<td>34.3±0.7</td>
<td>22.9±5.7</td>
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<tr>
<td>6</td>
<td>198</td>
<td>5.05-8.01</td>
<td>67</td>
<td>6.34±1.12</td>
<td>91.52±9.61</td>
<td>34.4±0.7</td>
<td>22.9±5.7</td>
</tr>
</tbody>
</table>
Table 3. Along-pier radium isotope average activities and one standard deviation for each weekly/monthly sampling event, n=5-6.

<table>
<thead>
<tr>
<th>Date</th>
<th>Ra-223 (dpm/L)</th>
<th>xsRa-224 (dpm/L)</th>
<th>Ra-226 (dpm/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-Apr-12</td>
<td>0.018 ± 0.004</td>
<td>0.164 ± 0.017</td>
<td>0.111 ± 0.013</td>
</tr>
<tr>
<td>17-Apr-12</td>
<td>0.015 ± 0.003</td>
<td>0.121 ± 0.017</td>
<td>0.092 ± 0.007</td>
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<tr>
<td>24-Apr-12</td>
<td>0.017 ± 0.004</td>
<td>0.139 ± 0.017</td>
<td>0.100 ± 0.010</td>
</tr>
<tr>
<td>1-May-12</td>
<td>0.013 ± 0.004</td>
<td>0.120 ± 0.024</td>
<td>0.091 ± 0.007</td>
</tr>
<tr>
<td>8-May-12</td>
<td>0.014 ± 0.002</td>
<td>0.111 ± 0.015</td>
<td>0.089 ± 0.005</td>
</tr>
<tr>
<td>15-May-12</td>
<td>0.016 ± 0.006</td>
<td>0.193 ± 0.012</td>
<td>0.108 ± 0.022</td>
</tr>
<tr>
<td>22-May-12</td>
<td>0.013 ± 0.003</td>
<td>0.142 ± 0.035</td>
<td>0.105 ± 0.016</td>
</tr>
<tr>
<td>29-May-12</td>
<td>0.014 ± 0.004</td>
<td>0.148 ± 0.022</td>
<td>0.098 ± 0.010</td>
</tr>
<tr>
<td>14-Jun-12</td>
<td>0.011 ± 0.003</td>
<td>0.118 ± 0.033</td>
<td>0.090 ± 0.015</td>
</tr>
<tr>
<td>19-Jun-12</td>
<td>0.010 ± 0.003</td>
<td>0.126 ± 0.061</td>
<td>0.085 ± 0.021</td>
</tr>
<tr>
<td>26-Jun-12</td>
<td>0.005 ± 0.003</td>
<td>0.062 ± 0.030</td>
<td>0.070 ± 0.009</td>
</tr>
<tr>
<td>3-Jul-12</td>
<td>0.008 ± 0.002</td>
<td>0.112 ± 0.036</td>
<td>0.100 ± 0.018</td>
</tr>
<tr>
<td>10-Jul-12</td>
<td>0.009 ± 0.002</td>
<td>0.116 ± 0.034</td>
<td>0.094 ± 0.017</td>
</tr>
<tr>
<td>24-Jul-12</td>
<td>0.043 ± 0.006</td>
<td>0.239 ± 0.025</td>
<td>0.148 ± 0.016</td>
</tr>
<tr>
<td>31-Jul-12</td>
<td>0.048 ± 0.005</td>
<td>0.238 ± 0.035</td>
<td>0.303 ± 0.068</td>
</tr>
<tr>
<td>7-Aug-12</td>
<td>0.054 ± 0.014</td>
<td>0.284 ± 0.061</td>
<td>0.366 ± 0.077</td>
</tr>
<tr>
<td>14-Aug-12</td>
<td>0.057 ± 0.014</td>
<td>0.295 ± 0.088</td>
<td>0.391 ± 0.079</td>
</tr>
<tr>
<td>30-Aug-12</td>
<td>0.022 ± 0.009</td>
<td>0.130 ± 0.049</td>
<td>0.178 ± 0.044</td>
</tr>
<tr>
<td>25-Sep-12</td>
<td>0.023 ± 0.004</td>
<td>0.147 ± 0.035</td>
<td>0.138 ± 0.021</td>
</tr>
<tr>
<td>18-Oct-12</td>
<td>0.014 ± 0.003</td>
<td>0.106 ± 0.014</td>
<td>0.127 ± 0.027</td>
</tr>
<tr>
<td>4-Dec-12</td>
<td>0.011 ± 0.002</td>
<td>0.095 ± 0.049</td>
<td>0.107 ± 0.020</td>
</tr>
<tr>
<td>15-Jan-13</td>
<td>0.008 ± 0.002</td>
<td>0.065 ± 0.012</td>
<td>0.098 ± 0.014</td>
</tr>
<tr>
<td>12-Feb-13</td>
<td>0.008 ± 0.004</td>
<td>0.082 ± 0.019</td>
<td>0.081 ± 0.016</td>
</tr>
<tr>
<td>2-Apr-13</td>
<td>0.009 ± 0.003</td>
<td>0.092 ± 0.030</td>
<td>N/A ± N/A</td>
</tr>
</tbody>
</table>
Table 4. Radium isotope and physical parameter analysis r-values from time-series sampling of bottom water at Station 6 on 7-May, 19-Jul, 4-Aug, 14-Aug, and 16-Aug; n=57, p<0.001, (n=51 for temperature).

<table>
<thead>
<tr>
<th></th>
<th>xsRa-224</th>
<th>Ra-223</th>
<th>Ra-226</th>
</tr>
</thead>
<tbody>
<tr>
<td>DO (mg/L)</td>
<td>0.816</td>
<td>0.887</td>
<td>0.894</td>
</tr>
<tr>
<td>DO Saturation (%)</td>
<td>0.878</td>
<td>0.787</td>
<td>0.894</td>
</tr>
<tr>
<td>Salinity (‰)</td>
<td>0.799</td>
<td>0.801</td>
<td>0.792</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>0.871</td>
<td>0.857</td>
<td>0.871</td>
</tr>
</tbody>
</table>

*excludes 17-May-2012 time-series sampling event

Table 5. Percentage of groundwater composition (%), residence time (days) from $^{223}$Ra and $^{224}$Ra$_{xs}$, observed average dissolved oxygen concentration (mg/L), and calculated dissolved oxygen concentration (mg/L) for samples taken on 4-, 7-, 14-, and 16-Aug-2012.

<table>
<thead>
<tr>
<th>%GW</th>
<th>Ra-223 Res. Time</th>
<th>xsRa-224 Res. Time</th>
<th>Observed DO</th>
<th>Calculated DO</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Aug</td>
<td>6.77±2.18</td>
<td>3.38±4.08</td>
<td>4.81±1.51</td>
<td>5.60±0.12</td>
</tr>
<tr>
<td>7-Aug</td>
<td>8.04±2.43</td>
<td>5.54±3.67</td>
<td>5.73±1.03</td>
<td>5.17±0.76</td>
</tr>
<tr>
<td>14-Aug</td>
<td>9.43±1.50</td>
<td>10.86±3.99</td>
<td>8.41±1.35</td>
<td>4.79±0.36</td>
</tr>
<tr>
<td>16-Aug</td>
<td>47.92±10.21</td>
<td>17.17±3.73</td>
<td>13.97±1.25</td>
<td>3.27±0.66</td>
</tr>
</tbody>
</table>
Figure 1. Map of Long Bay, South Carolina. Star represents approximate location of Apache Pier (33°45′41″ N, 78°46′47″ W). Inset shows aerial photograph of Apache Pier.
Figure 2. Aerial photograph of Apache Pier in Long Bay, SC. Numbers on pier show approximate locations of sampling stations.
Figure 3. Bottom water physical parameter averages for each sampling station during oxic weekly/monthly sampling efforts. Error bars represent one standard deviation from the mean.
Figure 4. Radon and radium isotope averages (dpm/L) for each sampling station during oxic weekly/monthly sampling efforts. Error bars represent one standard deviation from the mean.
Figure 5. Seasonal radon and radium isotope activities (dpm/L) per station during oxic sampling conditions.
Figure 6. Linear correlation plot of (A) $^{226}$Ra (dpm/L), (B) $^{223}$Ra (dpm/L), and (C) $^{226}$Ra (dpm/L) with oxygen saturation (%) of bottom water at Apache Pier during five time-series sampling events at Station 6. $R^2 = 0.619, 0.771, 0.799$, respectively (n=57).
Figure 7. Average radium isotope average activities (dpm/L) during oxic and hypoxic conditions. Error bars represent one standard deviation from the mean.
Figure 8. Bottom water oxygen saturation (%) and radon activity (dpm/L).


$R^2=0.492$, $n=407$, $p<0.001$. Data from the continuous monitoring station located on the end of Apache Pier.
**Figure 9.** Vertical water column profile of radium isotope activities (dpm/L), dissolved oxygen concentration (mg/L), and temperature (°C) taken at Station 6 on 17-Aug-2012.
Figure 10. Average radium isotope activities (dpm/L) from five beachface groundwater sampling events and bottom water hypoxic event. Error bars represent one standard deviation from the mean.
Figure 11. Ra-228 and $^{226}$Ra (dpm/L) activity ratios from ten offshore wells (Moore and Wilson, 2005; Moore, unpubl. data) and 16-Aug-2012 hypoxic samples.
Figure 12. Ra-228 and $^{226}$Ra activity ratios from Well A, Well LW, Well R, and 16-Aug-2012 hypoxic samples. $R^2 = 0.919$, $n=53$, $p<0.001$. 
Figure 13. Wind data from 1-Jul-2012 through 19-Aug-2012. Wind speed (m/s) and direction taken from the weather station on Apache Pier.
Figure 14. Residence time (days) of 4-Aug, 7-Aug, 14-Aug (shown in black), and hypoxic 16-Aug (shown in red) samples based on percentage of groundwater ($%_{gw}$) and $^{223}$Ra activities (dpm/L). $R^2=0.999$, n=3, p<0.001 for 4-, 7-, and 14-Aug-2012.
Figure 15. Residence time (days) of 4-Aug, 7-Aug, 14-Aug (shown in black), and hypoxic 16-Aug (shown in red) samples based on percentage of groundwater ($%_{gw}$) and $^{224}$Ra$_{xs}$ activities (dpm/L). $R^2=0.998$, n=3, p<0.001 for 4-, 7-, and 14-Aug-2012.
Figure 16. Observed and calculated dissolved oxygen concentrations (mg/L) for 4-, 7-, 14-, and 16-Aug-2012. Error bars represent the standard deviation from the mean. Values above the marked bars represent average percent composition of groundwater used for calculated concentrations.