A new perspective on coastal hypoxia: The role of saline groundwater

Richard N. Peterson^{a*}, Willard S. Moore^b, Sarah L. Chappel^a, Richard F. Viso^a, Susan M. Libes^a,
Leigha E. Peterson^a

^a School of Coastal and Marine Systems Science, Coastal Carolina University, Conway, South Carolina, USA

^b Department of Earth and Ocean Sciences, University of South Carolina, Columbia, South Carolina, USA

* Corresponding author: R. N. Peterson, School of Coastal and Marine Systems Science, Coastal Carolina University, Conway, SC 29528, USA (rpeters2@coastal.edu)

Abstract

Processes leading to the development of coastal hypoxia are usually attributed to anthropogenic nutrient loading. We present new evidence documenting a natural process capable of producing large-scale water masses undersaturated with respect to dissolved oxygen, independent of human-caused nutrient loading and subsequent nutrient-enhanced productivity. Along the heavily developed coastline of Myrtle Beach, South Carolina, the offshore discharge of saline, anoxic groundwater generates undersaturated bottom water masses which can be advected into nearshore waters. Highly elevated radium isotope activities measured in low-oxygen bottom waters cannot be supported by any known terrestrial source. Rather, discharge of cold, anoxic, high-radium water from offshore carbonate aquifers is the likely source. Density stratification inhibits mixing of these discharged waters during inshore transport. During a low-oxygen event in August 2012, this restricted mixing is likely the mechanism for the observed oxygen deficit in bottom waters. This discovery suggests benthic layers undersaturated with respect to dissolved oxygen may be considerably more prevalent than currently recognized, particularly around the carbonate-platform of the US east coast.

Key words: groundwater, hypoxia, radium, oxygen

Introduction

Severe dissolved oxygen (DO) depletion in coastal waters, a condition known as hypoxia, occurs in varied environments (Rabalais et al., 2010). The threshold for hypoxia is defined by the SCOR Working Group 128 to occur when dissolved oxygen concentrations drop below 62.5 μM (equivalent to 2 mg/L, 1.4 mL/L, or approximately 30% saturation; Levin et al., 2009; Rabalais et al., 2010; Zhang et al., 2010). In unrestricted coastal waters, hypoxia is most often attributed to nutrient-induced eutrophication (Diaz and Rosenberg, 2008; Rabalais et al., 2010). Nutrient sources may be local discharge of sewage, stormwater, or rivers draining excessively fertilized agricultural and municipal landscapes. Once in the coastal ecosystem, nutrients facilitate development of phytoplankton blooms. Under stratified conditions, the settling, consumption, and decay of this organic matter promotes significant DO depletion in bottom waters that are unable to rapidly exchange oxygen with the atmosphere (Diaz and Rosenberg, 2008). Reduced DO concentrations negatively impact benthic and pelagic macrofauna and at the extreme, can cause extensive regional-scale ‘dead zones’ (Rabalais et al., 2002).

Zhang et al. (2010) characterize three major types of coastal ecosystems in which hypoxia is known to occur. The first type is in the receiving waters of a large river estuary (e.g., Mississippi River, Chesapeake Bay, and Yangtze River), where terrestrial nutrient loading combined with salinity-driven stratification can produce episodic and/or periodic hypoxic events. Another type of hypoxia occurs in semi-enclosed basins (e.g., Baltic and Black Seas, fjords), where water exchange with the open ocean (and therefore flushing) is limited, magnifying the effects of nutrient loading into hypoxic events that may be persistent. Finally, coastal hypoxia may occur at sites of oceanic upwelling, normally where western boundary currents impinge on narrow continental shelves, allowing elevated nutrient concentrations in these upwelled water

masses to produce seasonal hypoxic events (Zhang et al., 2010). In each of these cases, oxygen may be consumed from both the water column and the sediments (Rabalais et al., 2010). The relative importance of benthic respiration has been shown to vary seasonally and inter-annually, but may dominate over water column respiration in some instances (Ostrom et al., 2005; Quiñones-Rivera et al., 2007, 2010; Wang et al., 2008).

Diaz and Rosenberg (2008) document a recent increase in recognized magnitude, frequency, and spatial extent of coastal hypoxia. These changes are largely attributed to anthropogenic nutrient loading through runoff and atmospheric inputs and often require a combination of biological (e.g., net respiration) and physical (e.g., stratification) mechanisms to reduce dissolved oxygen concentrations and maintain them at low levels.

Long Bay, South Carolina, (Figure 1) is one such coastal setting where episodic hypoxic conditions have been recognized since 2004. Long Bay is a concave embayment, stretching 160 km from Winyah Bay, South Carolina, to the Cape Fear River estuary, North Carolina. The center of Long Bay houses the Grand Strand – a highly urbanized stretch of beach containing the tourist center of Myrtle Beach.

Following the discovery of hypoxic conditions, continuous measurements of water quality parameters were initiated in surface and bottom waters at the seaward end of Apache fishing pier (Figure 1), about 250 m offshore where water depths range from 5 to 7 m (Libes and Kindelberger, 2010). Two additional piers were similarly instrumented in 2012, providing spatial coverage of approximately 35 km along the coastline of Long Bay (Libes et al., 2014).

Collectively, these observations document that the nearshore waters are characterized by short periods (hours to days) of low DO saturation in bottom water, often reaching hypoxic conditions,

82 especially in August and September. The events of longest duration and lowest DO occur during
83 and immediately after periods of sustained upwelling-favorable SW winds (Sanger et al., 2012).

84 The occurrence of low-DO conditions in Long Bay perplexed investigators, as it did not
85 follow the generally-accepted environmental types outlined by Zhang et al. (2010). Two
86 substantial river systems discharge at the edges of the bay, but their biogeochemical influence on
87 central Long Bay is not well understood. Moreover, the geomorphology of Long Bay does not
88 limit exchange and flushing with the ocean. Studies have demonstrated the potential for
89 upwelling to transfer deeper ocean water onto the continental shelf of Long Bay (Sanay et al.,
90 2008; Sanger et al., 2012), but this upwelled water would have to transit a long (100 km),
91 shallow continental shelf before reaching nearshore waters. Attempts to document the spatial
92 distribution of a hypoxic water mass in 2009, however, determined the low-DO waters to be
93 isolated to within 2 km of the shoreline and directly offshore of the most urbanized shoreline
94 (Sanger et al., 2012). No observations of reduced DO concentrations have been made beyond ~2
95 km from the shoreline, suggesting a localized, terrestrial source of the water quality
96 degradations, or that such low-DO water masses were simply missed during sampling.

97 Investigators initially speculated that the hypoxic events were related to the engineered
98 modification of stormwater pathways from the urbanized areas. Such modifications have aimed
99 to better convey runoff to the coastal waters through outfall pipes and channelized tidal creeks.
100 However, attempts to correlate rainfall events to the onset of hypoxic conditions have remained
101 unsuccessful.

102 During a 2009 hypoxic event, however, McCoy et al. (2011) detected anomalously high
103 activities of radon-222 (a tracer of groundwater discharge; see reviews by Burnett et al., 2006;
104 Swarzenski, 2007; Charette et al., 2008) in bottom waters that were 5-6 fold higher in

concentration than normal levels in this area. Radon activities subsided to background concentrations as DO concentrations increased throughout the tidal cycle. Radon also varied inversely with bottom water temperatures during these observations. These authors speculated that they sampled an admixture of groundwater (high radon, low oxygen, low temperatures) and ocean water (low radon, high oxygen, high temperatures) during this hypoxic event. As coastal groundwaters generally contain elevated nutrient concentrations (D'Andrea et al., 2002; Santos et al., 2008; Slomp and Van Cappellen, 2004) due to the mobilization of diagenetically-released biogeochemical constituents, the discharge of groundwater has been shown to contribute to ecosystem shifts (Lapointe, 1997), harmful algal blooms (Lee and Kim, 2007; Lee et al., 2010), and hypoxia (McCoy et al., 2011).

McCoy et al. (2011) speculated that the radon observations suggested a trapping mechanism, where an observed onshore-moving oceanic water mass prevented the dispersion of terrestrial runoff waters, leading to concentration of radon and nutrients from groundwater and runoff inputs to the nearshore zone. The typically abrupt concurrent declines in DO and temperature in Long Bay suggest an important role of advective transport, as fluctuations in these parameters are too rapid to be explained by biological processes at the monitoring stations (McCoy et al., 2011). These authors hypothesized that as this oceanic front trapped terrestrial materials in the nearshore, subsequent tidal oscillations allowed this enriched nearshore water mass to migrate back and forth past the stationary monitoring site, creating the observed rapid fluctuations in DO, temperature, and radon concentrations. This hypothesis, however, was based on a limited data set collected during and following a singular hypoxic event, and hence requires further evidence for testing as it may not represent the true nature of Long Bay oxygen dynamics.

The objectives of our work are to incorporate additional tracers of groundwater input to identify the sources of groundwater associated with Long Bay DO fluctuations. We ultimately provide an alternative hypothesis to that proposed by McCoy et al. (2011) by showing that the driver of Long Bay oxygen dynamics are not controlled by nearshore processes, but rather the discharge of cold, anoxic, saline groundwater from offshore aquifers. Periodic pier-based measurements of radium isotopes throughout 2012 serve as additional tracers of groundwater discharge and offer a means to provide age information on abnormally low-DO waters. The quartet of naturally-occurring radium isotopes (^{223}Ra , ^{224}Ra , ^{226}Ra , and ^{228}Ra) has a wide range of radioactive half-lives (11.4 days, 3.6 days, 1600 years, and 5.7 years, respectively), and have been used to estimate ages of coastal waters and fluxes of submarine groundwater discharge (Moore, 1996; Moore, 2000a; Peterson et al., 2008).

Methods

Hydrographic Measurements

Continuous measurements of water depth, salinity, temperature, DO concentration and % saturation (a relative measure of oxygen concentration compared to the temperature- and salinity-dependent solubility capacity) were conducted from the seaward end of Apache Pier (Figure 1) throughout 2012 using YSI 6600 sondes deployed in the bottom (~1m above the seabed) and surface (~ 1m below the air-sea interface). These sondes were calibrated for all parameters weekly, and measurements were validated during weekly visits using an independent sonde following recommendations in USIOOS (2015). Additionally, periodic vertical profiles (1-m vertical increments) of these parameters were recorded at six stations along the length of Apache Pier using a YSI Pro30 handheld conductivity/salinity meter (with a reported accuracy in

salinity values of ± 0.1) and a YSI ProODO dissolved oxygen meter (with a reported accuracy of $\pm 1\%$ of the measured dissolved oxygen saturation value). These data were imported into MATLAB to construct 2-dimensional contour plots to visualize vertical and lateral stratification in the nearshore waters. An onsite weather station recorded meteorological conditions, including air temperature, wind speed/direction, barometric pressure, and rainfall at a height of approximately 10 m above sea level.

Radium Isotope Measurements

Radium isotopes were sampled from six stations located longitudinally along the length of Apache Pier from April 2012 through April 2013. These sampling efforts were designed to assess the spatial variability of radium isotopes in bottom waters along shore-normal transects from the high-tide line through the surf zone and into the nearshore waters. The sampling efforts also captured spring/neap variability through the summer in Long Bay (i.e., weekly sampling frequency during the spring and summer when the most pronounced DO fluctuations are expected; monthly sampling frequency during the fall and winter seasons). During times of reduced DO concentration, hourly time-series sampling of radium isotopes in bottom waters was conducted from the end of Apache Pier to assess tidal variability. Additionally, groundwater samples were analyzed for their radium isotopic signatures from wells inserted in the beachface as well as offshore wells in a karstic, carbonate aquifer (Moore et al., 2002; Moore and Wilson, 2005).

Radium isotopes were sampled by pumping large volumes (60-L) of ocean water into a carboy. Groundwater samples (3-6 L) were collected from PVC wells inserted into the beachface (McCoy et al., 2011) and offshore aquifers (Moore et al., 2002; Moore and Wilson, 2005). One

PushPoint profile of pore waters was collected just offshore Myrtle Beach in 2013 as described by Moore et al. (2006). Turbid groundwater samples were allowed to settle for 3-6 hours and decanted prior to processing. The samples were filtered through acrylic fibers impregnated with MnO₂ (Moore, 1976; Moore and Reid, 1973) to quantitatively extract dissolved radium isotopes. The short-lived ²²³Ra and ²²⁴Ra adsorbed on the Mn-fibers were measured on a Radium Delayed Coincidence Counter (RaDeCC; Moore and Arnold, 1996) immediately after collection, and again after three weeks to correct for the amount of ²²⁴Ra supported by adsorbed ²²⁸Th to yield ‘excess ²²⁴Ra’. The minimum detectable activities for this method were 0.004 dpm/L for ²²³Ra and 0.020 dpm/L for ²²⁴Ra. Measurement uncertainties (1-σ) for data reported herein averaged 11.3% (± 5.7%) and 3.4% (± 1.4%) of measured values for ²²³Ra and ²²⁴Ra, respectively. Ra-226 was analyzed by ingrowth of its daughter, ²²²Rn, via RaDeCC (Peterson et al., 2009; Waska et al., 2008) and confirmed via gamma spectroscopy, which also provided measurements of ²²⁸Ra (Moore, 1984) in selected samples. Minimum detectable activities for ²²⁶Ra analysis were 0.022 dpm/L and 1-σ measurement uncertainties averaged 2.1% (± 0.8%) of measured values for data reported here.

Results

Bottom water dissolved oxygen and temperature records collected throughout 2012 from Apache Pier reflect dynamic fluctuations that occur on relatively rapid time-scales (Figure 2A). Throughout the continuous monitoring data set from 2012, DO percent saturations averaged 92%, ranging from 37 to 120% (equivalent to a range from 74 to 266 μM O₂). Throughout this manuscript, we primarily report DO concentrations in terms of % saturation to remove the impact of the temperature- and salinity-dependent solubility coefficient. Though these

concentrations never reached the defined threshold for hypoxia ($< 65 \mu\text{M}$; $\sim 30\%$ saturation), substantial excursions toward undersaturation occurred frequently, particularly during the late spring and summer.

From 10 April 2012 through 2 April 2013, radium isotopes were measured along the length of Apache Pier (Figure 3). Ra-226 activities were in the range $0.07 - 0.14 \text{ dpm/L}$ (average of $0.12 \pm 0.03 \text{ dpm/L}$) except for samples collected from 31 July 2012 - 31 August 2012. Samples during this period ranged from $0.16 - 4.0 \text{ dpm/L}$ (average of $1.63 \pm 1.35 \text{ dpm/L}$). The short-lived isotopes (^{223}Ra and ^{224}Ra) followed a similar pattern with somewhat lower degrees of enrichments during 31 July 2012 - 31 August 2012. During most of the time series, $^{224}\text{Ra}_{\text{xs}}$ activities were somewhat higher than ^{226}Ra except for the period between 31 July 2012 and 31 August 2012, when ^{226}Ra activities exceeded $^{224}\text{Ra}_{\text{xs}}$. This data set demonstrates a statistically significant inverse relationship between DO % saturation and radium isotope activities (Figure 4).

From 16-17 August 2012, the bottom water sonde recorded abnormally low dissolved oxygen conditions (DO levels reached 41% saturation, or $83 \mu\text{M}$ at 2:30 am on 17-Aug-2012) at Apache Pier, corresponding with concurrent declines in water temperature and elevated salinities (Figure 2B). This low DO event was similarly recorded at two other instrumented fishing piers in Long Bay, indicating the processes affected a length of at least 35 km of coastline. This event occurred during predominant SW winds following a sustained period of low magnitude W winds (Figure 5).

Leading up to the onset of this event, the water column along the length of Apache Pier (particularly bottom waters) became progressively cooler (from 30°C to 28°C) and salinities increased from 34 to 36 (Figure 6). During this period, we increased our radium isotope

sampling frequency at Apache Pier. On 16 August, a bottom water sample had extremely high radium activities, up to 4 dpm/L for ^{226}Ra and 7 dpm/L for ^{228}Ra . On 17 August, a depth profile of the 7 m water column at the end of the pier revealed a low-temperature, low-DO water layer in the bottom 2 m containing abnormally high ^{226}Ra and ^{228}Ra activities (up to 3.2 and 4.9 dpm/L, respectively; Figure 7). Surprisingly, ^{223}Ra and ^{224}Ra activities of these samples collected under reduced DO levels were considerably lower (0.3-0.6 dpm/L for ^{224}Ra and 0.1-0.2 dpm/L for ^{223}Ra) than the ^{226}Ra and ^{228}Ra activities. Nevertheless, these values were a factor of 2-3 higher in ^{224}Ra , and 10-20 times higher in ^{223}Ra relative to values measured earlier in the summer when dissolved oxygen was fully saturated.

To put these activities into perspective, open ocean surface values for ^{226}Ra are 0.075 ± 0.015 dpm/L (Broecker and Peng, 1982); high values in the coastal ocean may reach 0.3 dpm/L. For ^{228}Ra , coastal values may reach 0.6 dpm/L (Moore, 2000b; Moore et al., 2008). During May 2012, when DO conditions concentrations were fully saturated, we measured ^{226}Ra activities of 0.16 dpm/L and ^{228}Ra activities of 0.17 dpm/L in these bottom waters (Figure 3). Values for the lower-DO bottom waters were over 30 times greater than the May values when oxygen was fully saturated, and over an order of magnitude higher than any such values reported in the literature from coastal marine systems (Moore, 2010a).

In addition to the pier measurements, we measured ^{226}Ra and ^{228}Ra activities in many environments surrounding Long Bay, including beachface porewaters, the Intracoastal Waterway behind Myrtle Beach, numerous rivers and river plumes (including Little River Inlet) along the coast, fresh groundwater in deep aquifers, and several offshore monitoring wells (Figure 8). With the exception of the offshore monitoring wells (Wells A, R, J, 1, 2, and PushPoint sampler as shown in Figure 1), the other environments had ^{226}Ra activities in the range 0.1-0.5 dpm/L and

^{228}Ra in the range 0.1 – 0.7 dpm/L, considerably lower than the high activities reported here for bottom waters under Apache Pier.

The offshore wells, by contrast, had ^{226}Ra activities in the range 1-10 dpm/L and ^{228}Ra activities in the range 1-12 dpm/L (Moore et al., 2002; Moore and Wilson, 2005). These wells (2-4 m deep into the bottom sediments in 15 m water depth; Figure 1) were set through sand and clay layers to just above a limestone basement (Moore et al., 2002). Water from these wells has consistently been salty, anoxic, $\sim 4^\circ\text{C}$ cooler than ambient bottom waters during the late summer, and strongly enriched in radium isotopes (Moore et al., 2002; Moore and Wilson, 2005). Results from a PushPoint profile collected just offshore of Myrtle Beach had activities of ^{226}Ra and ^{228}Ra of around 8 dpm/L, similar to activities measured in the wells (Figure 8C).

Discussion

The undersaturated DO water mass measured at Apache Pier on 16-17 August 2012 was enriched in ^{226}Ra and ^{228}Ra by about an order of magnitude compared to fully-oxygenated bottom waters measured earlier in the summer. The offshore wells provide the only endmember samples we have measured that are high enough in ^{226}Ra and ^{228}Ra to support activities found in the bottom waters undersaturated with respect to oxygen. The offshore wells are characterized by unique $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratios (AR's), with two wells (Wells A and R; Table 1) having almost exactly the $^{228}\text{Ra}/^{226}\text{Ra}$ AR as measured in the lower-DO samples collected from Apache Pier (Figure 8C). Activities in the PushPoint samples collected closer to Myrtle Beach were similar to these wells (Figure 8C). Additionally, the water sampled from these wells is anoxic and relatively cold with high salinity as compared to the overlying surface waters, similar to the

measurements of bottom water at the pier during the period when DO saturation was less than 60%.

All of these features suggest that submarine groundwater discharge (SGD) from offshore aquifers containing water with properties similar to monitoring wells A and R and the PushPoint profile made up a significant component of the undersaturated water mass measured under Apache Pier on 16-17 August 2012. Moore and Wilson (2005) discuss several mechanisms by which groundwater from this offshore sediment and carbonate aquifer system can discharge into the overlying seawater. Tidal pumping due to fluctuating pressure heads (see review by Santos et al. 2012a) drives shallow porewater exchange throughout the year, whereas sediment porewater flushing is also shown to occur during storm events from wave forces. Most notably, Moore and Wilson (2005) document buoyancy-driven flushing of sediment porewater when the overlying water column cools (such as during upwelling-driven circulation), stimulating upward advection of warmer groundwater from the carbonate aquifer.

The SGD would produce a thin bottom layer of cold, high salinity, low oxygen water highly enriched in radium isotopes. During the relatively calm conditions (low magnitude W winds; Figure 5) preceding the low-DO event, we suspect that density stratification between this cold, salty layer and the surrounding ambient ocean waters was established, which would likely inhibit further mixing and maintain this layer as a semi-coherent water mass. This SGD layer would likely then be forced shoreward when prevailing S-SW winds began again on 10 August 2012 (Figure 5) which caused upwelling at the shelf break [as described by Sanay et al. (2008)]. We suspect that this onshore migration of bottom waters combined with tidal currents (particularly during spring tide) are capable of pushing this bottom water layer to the nearshore waters where they can be observed at Apache Pier.

We use a 2-endmember mixing model to estimate the fraction of the benthic water mass composed of an original groundwater signature by the time of its arrival in the nearshore waters of Long Bay. For this, we assume offshore, karstic groundwater represented by Wells A and R (Figure 8C) mixes with ambient ocean water as the only sources contributing to the radium isotope concentration within the benthic water mass and that the endmember composition is constant over time. Additionally, using the long-lived ^{228}Ra and ^{226}Ra in such an endmember mixing model allows us to neglect the effects of radioactive decay on these time scales after discharge. The following equations are solved simultaneously, and independent estimates can be derived using each of the long-lived isotopes:

$$f_{GW} + f_{SW} = 1 \quad 1$$

$$Ra_{GW}f_{GW} + Ra_{SW}f_{SW} = Ra_{Low-DO} \quad 2$$

where f_{GW} and f_{SW} represent the fraction of the benthic, lower-DO water mass composed of groundwater and surface water, respectively; Ra_{GW} and Ra_{SW} represent the endmember activities of radium in the groundwater and surface water, respectively; and Ra_{Low-DO} is the measured radium activity in the bottom waters from Apache Pier during the low-DO event.

Based on this mixing model, we find that during the 16-17 August 2012 low-DO event, the bottom water at Apache Pier was composed of between 30 and 60% groundwater by volume (see Table 2). To put these values into context, Moore (2010b) estimated an annual SGD flux into continental shelf waters along the South Atlantic Bight of $1.2 \times 10^{12} \text{ m}^3$ (distributed over an area of $6 \times 10^{10} \text{ m}^2$). Given that the residence time of these waters is on the order of a month (Moore, 2007), this SGD flux represents a steady-state flux of $1 \times 10^{11} \text{ m}^3/\text{mo}$, or a standing stock of 1.67 m^3 of groundwater per m^2 of seabed. If we take an average water depth of 20 m through this region (which would represent a total water volume of $20 \text{ m}^3/\text{m}^2$ of seabed), the

standing stock of groundwater would comprise 8.3% of the continental shelf water volume. This estimate assumes the SGD is thoroughly mixed throughout these waters, whereas our estimates of 30-60% of the water volume during this low-DO event being comprised of groundwater results from a lack of dispersal mixing.

Based on these mixing results, simply mixing anoxic groundwater with oxic surface water in this bottom water mass is sufficient to account for the reduced DO concentration in this layer (Table 2). There is no requirement for additional biological oxygen demand during the low-DO event reported here, as conservative mixing alone is sufficient to account for the reduced DO concentrations. This is a conservative estimate of the effect of the groundwater on DO, because we assign the groundwater a O_2 content of 0 μM , although it is in effect negative because of a chemical oxygen demand that would result from oxidizing the elevated sulfide content after its discharge into the bottom water. This is a case where dissolved oxygen dynamics along a heavily-developed coastline do not seem to be dependent upon anthropogenic nutrient fluxes or biological respiration, but rather natural physical processes. Clearly, more research is needed to examine the cumulative DO budget from a biological perspective from the time of discharge to arrival in the nearshore waters of Long Bay.

The short-lived radium isotopes can be used to infer the transport time of this water mass from its region of origin offshore into the nearshore waters of Long Bay, as substantial radioactive decay occurs over the transit time scale. Normalizing a short-lived radium isotope (e.g., ^{224}Ra) to a long-lived isotope (e.g., ^{226}Ra) accounts for effects of mixing, so any deficit of this AR below the source endmember AR is due to decay of the short-lived isotope (Moore, 2000a). The average initial $^{224}Ra/^{226}Ra$ AR for Well A is 2.26. A plot of ^{224}Ra versus ^{226}Ra for

the bottom waters undersaturated in oxygen indicates a $^{224}\text{Ra}/^{226}\text{Ra}$ AR of 0.11 (Figure 9A).

Using the relationship proposed by Moore (2000a):

$$t = \text{Ln} \left[\frac{\left(\frac{^{224}\text{Ra}}{^{226}\text{Ra}} \right)_{\text{measured}}}{\left(\frac{^{224}\text{Ra}}{^{226}\text{Ra}} \right)_{\text{initial}}} \right] \cdot \frac{1}{\lambda_{226} - \lambda_{224}}$$

where the measured AR in the water mass is compared to the initial AR of the source water

(Well A), and λ represents the decay constants of each isotope. Assuming no additional sources

of ^{224}Ra to this water mass during transit, the estimated minimum transit time is between 13 and

15 days (Table 3). The parent of ^{224}Ra , ^{228}Th , is expected to be present in bottom sediments and

may contribute ^{224}Ra via diffusion to bottom waters during transport; thus, the apparent age of

these samples represents a minimum estimate. Transit time estimates based on ^{223}Ra are

somewhat higher, ranging from 22 to 31 days (see Table 3), probably because of lower parent

activity for ^{223}Ra (^{227}Ac) than ^{224}Ra in the sediments (Levy and Moore, 1985). These transit time

scales are consistent with periods of upwelling-favorable winds in this region (Sanay et al., 2008)

and likely require spring tidal currents to reach the nearshore waters of Long Bay.

These estimates are based on the assumptions that (1) no other sources of radium besides

SGD, and (2) no other sinks of radium besides mixing and radioactive decay affect this benthic

water mass. As discussed above, diffusion of ^{224}Ra from bottom sediments may inject this

isotope to the benthic water mass. Additionally, the presence of a cold, salty water mass

overlying the sediments may drive shallow porewater exchange into the bottom waters via salt

fingering and density-driven convection (Rocha, 2000; Santos et al., 2012b). Such exchange

would also add radium isotopes to the bottom water mass. However, such exchange processes

would likely preferentially add more of the short-lived radium isotopes due to their more rapid

production in the sediments. Given that the short-lived radium isotopes demonstrate much less enrichment in this benthic water mass (Figure 3) leads us to reject continued porewater exchange during inshore transport as a significant source of radium to these waters.

In contrast to the hypothesis of McCoy et al. (2011) that the dominant source of groundwater associated with dissolved oxygen depletions off Myrtle Beach was of terrestrial origin, the results presented here indicate rather that offshore discharge of groundwater from a karstic aquifer is the source of the low-DO water mass in Long Bay. We acknowledge that these results are based on a single low-DO event which may not fully represent the driving forces of all such events in Long Bay. It is conceivable that different sources may contribute to dissolved oxygen fluctuations in this dynamic coastal system.

Our hypothesis raises a fundamental question: Why has this natural phenomenon been recognized only recently in Long Bay? One possibility is that some event has caused a recent change in the timing and rates of SGD. Another possibility is that low-oxygen, high-radium bottom waters have historically been present, but have remained undetected due to a lack of frequent or continuous observations in Long Bay across appropriate temporal and spatial scales. Only recently have investigators targeted near-bottom (<1 m) waters for DO measurements. Although Moore (Moore, 1996; Moore et al., 2008) reported hundreds of surface and deep water (>3 m above bottom) radium isotope measurements in the region during the period between 1994-2000, only one data set reported unusually high ^{228}Ra and ^{226}Ra activities in deep waters (Moore and Shaw, 1998). These values, however, were an order of magnitude lower than the results presented here.

Conclusions

In summary, results from a robust data set associated with a specific period of 21 days of undersaturated oxygen water (<60%) in the nearshore waters of Long Bay, SC, suggest that the mechanism causing low DO in the case reported here is from discharge of cold, salty, anoxic groundwater from limestone aquifers farther offshore. These waters retain 30 to 60% of the groundwater component during an approximately 2-3 week inshore transit. A conservative DO mass balance shows that mixing anoxic groundwater with oxic seawater can account for the DO deficit in this water mass. This set of conditions (cold, anoxic groundwater discharge along a flat carbonate continental shelf) is common along many coastlines (particularly passive margins) (Moore et al., 2008). Therefore, we speculate that similar benthic, low-DO water masses may be much more prevalent than are currently recognized.

The presence of SGD-impacted bottom water on the shelf may be more prevalent than data suggest, but it has simply not been sampled. Proof of our hypothesis will require discrete sampling of near-bottom waters during periods of depleted DO levels. The use of Eulerian or Lagrangian continuous sensors could assist immensely. Clearly, bottom waters in nearshore environments along the US east coast and elsewhere should not only be monitored for DO, but tracers of SGD should be measured as well to characterize the source(s) of the water. Finally, the potential for SGD to be a significant natural source of low-DO to nearshore bottom waters suggests that it could be an important agent limiting the assimilative capacity of these waters for anthropogenic inputs of oxygen-demanding materials that are typically supported by nutrient-enhanced productivity via stormwater and riverine inputs.

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Tables

Table 1. Salinity, ^{226}Ra , and ^{228}Ra values measured from Wells A and R.

		⁵⁵⁹ Ud	⁵⁵ : Ud
Vdp sdqj Gdwh	Vddqlw ^d	+gsp 20,	
Well A			
20-Jul-99	ND	6.05	9.93
24-Jul-99	ND	6.04	8.86
08-Sep-99	35	5.98	9.15
10-Sep-99	35.15	6.69	8.53
09-Nov-99	35.2	5.41	8.71
10-Nov-99	35.2	4.83	6.72
14-Nov-99	ND	4.65	7.23
14-Nov-99	ND	5.89	7.76
26-May-00	35.2	4.54	5.54
26-May-00	35.3	7.86	11.48
02-Jun-00	35.1	4.15	6.25
02-Jun-00	35.3	4.69	7.04
04-Jun-00	35.2	4.62	7.00
04-Jun-00	35.1	3.89	6.15
31-Aug-00	35.09	5.24	7.38
31-Aug-00	35.05	7.50	10.27
04-Sep-00	35.02	5.13	6.70
04-Nov-00	ND	4.85	5.97
04-Nov-00	ND	5.62	6.97
08-Nov-00	ND	4.60	6.08
07-Feb-01	35.9	2.75	3.64
07-Feb-01	35.6	2.91	4.87
07-Feb-01	35.6	3.76	5.01
07-Feb-01	35.9	3.19	4.27
23-Aug-01	35.2	3.52	4.82
09-Jul-02	34.4	6.31	8.14
09-Jul-02	34.4	6.47	8.36
31-Jul-03	34.8	6.32	8.54
31-Jul-03	34.7	6.06	8.45
25-Oct-04	34.8	6.67	8.87
25-Oct-04	35.0	5.31	7.06
09-Sep-13	35.15	5.44	8.23
Well R			
1-Sep-00	ND	10.04	12.47
4-Nov-00	ND	3.33	4.62
23-Aug-01	34.9	6.17	8.45
9-Jul-02	34.0	9.33	12.34

^a - 'ND' indicates no data available

Table 2. Benthic, depleted DO water mass decomposition analysis based independently on ^{226}Ra and ^{228}Ra for each time-series measurement. Endmembers used here are based on maximum radium activities in Well A to yield conservative estimates of f_{GW} . Values for predicted DO based on the mixing estimates are presented in concentration units (μM) rather than DO saturation. Each ~hourly time-series sampling date is separated into distinct sections.

Fr a h f w r q W p h	^{559}Ud Df w y l y t g s p D,	$^{55}\text{Ud}^d$ t g s p D,	f_{GW} 0559 ^e %	f_{GW} 055; ^f %	P h d v x u h g GR μP ,	S u h g l f w h g GR 0559 ^g μP ,	S u h g l f w h g GR 055; ^g μP ,
17 May 2012							
10:51	0.173	0.180	0.9	0.2	172	183	185
12:42	0.184	0.186	1.1	0.2	187	183	185
14:28	0.142	0.170	0.5	0.1	213	184	185
16:19	0.144	0.136	0.6	-	222	184	-
18:36	0.145	0.187	0.6	0.2	219	184	185
19 July 2012							
14:12	0.109	ND	0.1	-	207	185	-
15:12	0.098	ND	-	-	213	-	-
16:12	0.117	ND	0.2	-	207	185	-
17:12	0.119	ND	0.2	-	207	185	-
18:12	0.158	ND	0.7	-	206	184	-
19:12	0.110	ND	0.1	-	202	185	-
20:12	0.147	ND	0.6	-	199	184	-
21:12	0.136	ND	0.5	-	194	184	-
22:12	0.148	ND	0.6	-	193	184	-
04 August 2012							
0:02	0.241	ND	1.8	-	175	182	-
1:02	0.343	ND	3.1	-	178	179	-
2:02	0.283	ND	2.4	-	178	181	-
3:02	0.450	ND	4.5	-	179	177	-
4:02	0.267	ND	2.1	-	175	181	-
5:02	0.344	ND	3.1	-	175	179	-
6:05	0.347	ND	3.2	-	171	179	-
7:02	0.369	ND	3.5	-	169	179	-
14 August 2012							
13:02	0.403	1.008	3.9	7.5	163	178	171
13:32	0.443	1.198	4.4	9.1	151	177	168
14:02	0.466	1.028	4.7	7.6	156	176	171
14:32	0.342	1.246	3.1	9.6	133	179	167
15:02	0.394	1.057	3.8	7.9	146	178	170
Low-DO Event - 16 August 2012							
8:52	2.62	4.65	32.5	39.6	119	125	112
9:22	3.15	5.28	39.3	45.2	118	112	101
9:52	3.02	5.04	37.6	43.1	112	115	105
10:22	3.22	5.59	40.2	48.0	96	111	96
10:52	3.13	5.40	39.0	46.3	88	113	99
11:22	3.72	6.22	46.6	53.5	83	99	86
11:52	3.99	6.60	50.1	56.9	90	92	80
12:22	2.97	5.28	37.0	45.2	88	117	101
13:02	2.75	4.55	34.1	38.8	89	122	113
13:32	3.24	5.48	40.5	47.0	77	110	98
14:02	3.10	5.44	38.7	46.6	73	113	99
14:32	2.54	4.13	31.4	35.1	106	127	120
15:02	2.20	3.61	27.1	30.5	122	135	129
15:32	3.01	4.93	37.5	42.1	124	116	107
16:02	3.90	6.58	49.0	56.7	146	94	80

^a - 'ND' indicates no data available

^b - fraction of groundwater in benthic, low-DO water mass based on ^{226}Ra ; Endmembers: $Ra_{SW} = 0.100$ dpm/L, $Ra_{GW} = 7.86$ dpm/L

^c - fraction of groundwater in benthic, low-DO water mass based on ^{228}Ra ; Endmembers: $Ra_{SW} = 0.163$ dpm/L, $Ra_{GW} = 11.48$ dpm/L

^d - Predicted DO concentration in benthic, low-DO water mass, based on f_{GW-226} ; Endmembers: $DO_{SW} = 5.92$ $\mu\text{g/L}$; $DO_{GW} = 0$ mg/L

^e - Predicted DO concentration in benthic, low-DO water mass, based on f_{GW} ; Endmembers: $DO_{SW} = 5.92$ $\mu\text{g/L}$; $DO_{GW} = 0$ mg/L

550 Table 3. Transit time estimates based on the $^{224}\text{Ra}_{\text{XS}}/^{228}\text{Ra}$ and $^{223}\text{Ra}/^{226}\text{Ra}$ isotope ratios
 551 measured during the low-DO event on 16 Aug. 2012.

Frødhvåg Wp h	^{556}Ud	$^{557}\text{Ud}_{\text{v}}$	^{559}Ud	^{555}Ud	$^{557}\text{Ud}_{\text{v}}$	^{555}Ud	^{556}Ud	^{559}Ud
	Df wylv	Df wylv	Df wylv	Df wylv	Df wylv	Df wylv	Df wylv	Df wylv
Low-DO Event - 16 August 2012								
8:52	0.12	0.40	2.62	4.65	17.9			34.4
9:22	0.12	0.49	3.15	5.28	17.5			37.5
9:52	0.13	0.44	3.02	5.04	17.8			35.4
10:22	0.15	0.47	3.22	5.59	18.0			34.1
10:52	0.14	0.39	3.13	5.40	18.8			34.8
11:22	0.15	0.46	3.72	6.22	18.6			36.5
11:52	0.17	0.49	3.99	6.60	18.6			35.6
12:22	0.13	0.41	2.97	5.28	18.4			35.2
13:02	0.13	0.42	2.75	4.55	17.5			33.9
13:32	0.15	0.50	3.24	5.48	17.5			34.2
14:02	0.14	0.44	3.10	5.44	18.2			34.6
14:32	0.10	0.33	2.54	4.13	18.2			36.9
15:02	0.12	0.28	2.20	3.61	18.4			31.5
15:32	0.15	0.50	3.01	4.93	17.0			33.0
16:02	0.21	0.54	3.90	6.58	18.1			31.7

Figure Captions

Figure 1. Base map of Long Bay, SC, showing the developed urban center along the Grand Strand and Apache Pier (shown in inset C) where the low-DO water mass was sampled. Bathymetric contours are given in m below sea level. Offshore wells (Moore et al., 2002; Moore and Wilson, 2005) are set into sand and clay layers atop a carbonate basement. Radium data from Wells A and R are presented in Table 1 and Figure 8C. In Sept. 2013, a PushPoint sampler deployed closer to shore found water with shallow porewater Ra activities similar to those observed in Wells A and R.

Figure 2. (A) DO (green line), salinity (red line), and water temperature (blue line) time-series in bottom water measured from Apache Pier during 2012. (B) The same parameters during the low DO event in August 2012, with the gray line showing the tidal water level. Horizontal lines indicate the 60% oxygen saturation (dashed line), 50% oxygen saturation (dotted line), and 30% oxygen saturation ('hypoxic'; dotted/dashed line) levels. Data were measured every 15 minutes.

Figure 3. (A) ^{223}Ra , (B) excess ^{224}Ra , and (C) ^{226}Ra activities measured in bottom water at the offshore extent of Apache Pier, collected weekly from April 2012 through April 2013, and during higher frequency sampling tidal time-series during the low-DO event. The box highlights samples collected during the 16-17 August 2012 low-DO event.

Figure 4. Statistically significant inverse relationship between DO % saturation and ^{223}Ra (A; R^2 : 0.71; $p < 0.01$; $n=82$), $^{224}\text{Ra}_{\text{XS}}$ (B; R^2 : 0.52; $p < 0.01$; $n=82$), and ^{226}Ra (C; R^2 : 0.73; $p < 0.01$; $n=82$) from the samples measured throughout this study (radium data are from Figure 3).

Figure 5. Vector plot indicating wind speed and direction (as cardinal direction; north is up) preceding the low-DO event on 16-17 August 2012. Through August 2012, winds were predominantly from the S-SW, creating upwelling-favorable conditions (Sanay et al., 2008) in Long Bay. The low-DO event reported here occurred after a period of low-magnitude W winds, which we suspect did not mix the water column and therefore allowed thermal stratification of a cold layer undersaturated with respect to oxygen to form near the bottom. As the upwelling-favorable winds began on 10 August 2012, onshore migration of bottom waters forced this low-DO water mass toward the measurement station at Apache Pier.

Figure 6. Two-dimensional contour plots of water temperature (top panel), DO concentration (middle panel), and salinity (bottom panel) during the summer of 2012 preceding and during the low-DO event on 16-17 August 2012. Each set of three plots show the daily water column (vertical) distribution of these parameters along the length of Apache Pier (horizontal). In this configuration, the beach is on the left side of each plot, and offshore is on the right. Vertical profiles were measured at 1-m increments (black dots) from the bottom. The color scales during each sampling shown here are the same.

Figure 7. Vertical profile of DO, temperature, and long-lived radium isotopes from the seaward end of Apache Pier on 17 August 2012. The cold, benthic layer containing high radium activities and low DO % saturation was especially evident near the bottom 2 m during this event, but high Ra activities extended into the surface waters where DO and temperature are affected by the atmosphere. Temperature and DO profiles are typical of most observed low-DO events documented throughout Long Bay.

Figure 8. Cross-plots between the long-lived ^{228}Ra and ^{226}Ra isotope activities. (A) Radium activities measured in terrestrial source waters and bottom waters from Apache Pier during normal conditions (i.e., other than 16-17 August) in summer 2012. (B) Radium activities measured in bottom waters from Apache Pier during the low-DO event in August 2012. These values are an order of magnitude higher than data shown in A (encompassed within the dashed box in B; note different axis scales). The terrestrial endmember sources from beachface groundwater and the Little River plume are not capable of producing the high radium isotope activities measured in bottom waters during the undersaturated DO event. (C) Radium isotopes measured in waters from offshore wells installed just above the limestone basement (Moore and Wilson, 2005). Water from these formations is the only documented source capable of supporting the radium activities and activity ratios observed in the low-DO water mass.

Figure 9. Cross-plots between radium isotopes during the low-DO event of 16-17 August 2012: (A) $^{224}\text{Ra}_{\text{xs}}$ versus ^{226}Ra ; (B) $^{224}\text{Ra}_{\text{xs}}$ versus ^{228}Ra ; (C) ^{223}Ra versus ^{226}Ra ; and (D) ^{223}Ra versus ^{228}Ra .

Figure 2

Figure 3

Figure 4

Figure 7

Figure 9