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Groundwater Discharge: Potential Association with Fecal Indicator Bacteria in the Surf Zone

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Short-lived radium isotopes (^{223}Ra and ^{224}Ra) are used to investigate the potential association between groundwater discharge and microbial pollution at Huntington Beach, CA. We establish the tidally driven exchange of groundwater from the surficial beach aquifer across the beach face. Groundwater is found to be a source of nutrients (silica, inorganic nitrogen, and orthophosphate) to the surf zone, and these nutrients could possibly provide an environment for enhanced growth or increased persistence of fecal indicator bacteria (FIB). Ammonium and ortho-phosphate explain up to 12−20% of the variance in FIB levels in the surf zone. Elevated levels of FIB were only found in 1 of the 26 groundwater samples. However, FIB in the surf zone covary with radium at fortnightly, diurnal, and semi-diurnal tidal periods. In addition, radium accounts for up to 38% of the variance in log-FIB levels in the surf zone. A column experiment illustrates that *Enterococcus* suspended in Huntington Beach saline groundwater is not significantly filtered by sand collected from the field. This work establishes a mechanism for the subterranean delivery of FIB pollution to the surf zone from the surficial aquifer and presents evidence that supports an association between groundwater discharge and FIB.

Introduction

The Clean Water Act mandates that beaches in the United States receiving more than 50 000 visitors per year are tested for fecal indicator bacteria (FIB) including total coliform (TC), fecal coliform (FC), and *Enterococcus* (ENT). Although these organisms are not pathogens themselves, formal epidemiology studies document relationships between their concentrations and acute gastrointestinal illness in recreational beach users (*1*−*3*).

Huntington State Beach (33°38′ N, 117°59′ W), located in Orange County, CA, 70 km south of Los Angeles, has been plagued by elevated levels of FIB since the summer of 1999, when between 10 000 and 13 000 m of beach were closed for nearly 90 d by the Orange County Health Care Agency. The length of coastline most significantly impacted is located approximately 1800 m north-west of the Talbert Marsh and Santa Ana River outlets, 7500 m from an offshore wastewater outfall, and 450 m from a thermal outfall (stations 9 and 10, Figure 1). This particular contamination problem has the unique characteristic of being most severe during the nights of spring tides during the summer months (*4*).

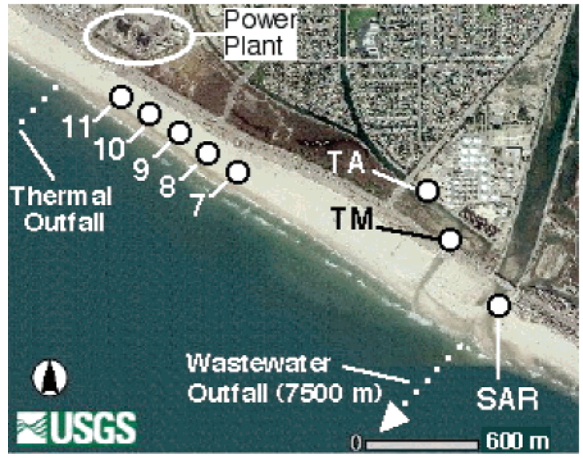

FIGURE 1. Map of the study site with sampling locations. SAR, TM, and TA stand for Santa Ana River, Talbert Marsh, and Talbert Aquifer sampling locations, respectively. Background is from the USGS seamless database. North is indicated by the large arrowhead in the lower left-hand corner.

Efforts to identify the source of the FIB to this beach have focused on the seasonal watershed outlets to the south (*5*−*7*), the treated wastewater plume offshore (*8*,*9*), and the thermal outfall (*10*). Studies show these are all potential sources of FIB but do not present an obvious, direct link to FIB levels at stations 9 and 10. One potential influence on surf zone water quality that has not been studied is groundwater discharge from the surficial unconfined aquifer. It is well-known that terrestrial groundwater can transport pathogens through the subsurface between leaking septic tanks and drinking water wells (*11*). In Florida, Paul et al. (*12*) demonstrated subsurface transport of coliphage from terrestrial subsurface sewage injection sites to coastal marine waters. Tidal pumping plays a role in the exchange of groundwater with the coastal ocean (e.g., refs *13*−*15*), and thus, the strong spring tide FIB signal at Huntington Beach might be consistent with tidally pumped groundwater.

There are at least two mechanisms by which groundwater may influence FIB concentrations at the beach. The first requires the beach water table to be seeded with FIB from leaking subterranean sewage lines or contaminated infiltrate and subsequently exchanged with seawater at the land−sea interface. At Huntington Beach, this mechanism demands the transport of FIB through porous media over at least 100 m, the distance between the surf zone and the nearest sewage infrastructure. The second possibility requires that groundwater possess unique chemical characteristics such as high nutrient or dissolved organic matter concentrations that, when discharged into seawater, prolong the persistence of FIB or instigate their growth (*16*). Both possibilities necessitate exchange between the surficial aquifer and the surf zone.

Figure 2 shows the subsurface hydrologic setting at the field site. The sketch on the right conceptualizes the surficial saline and brackish aquifers at our field site and their hypothesized interactions with each other and the surf zone. Although Huntington Beach has a Mediterranean climate with a distinctive dry season lasting from May through

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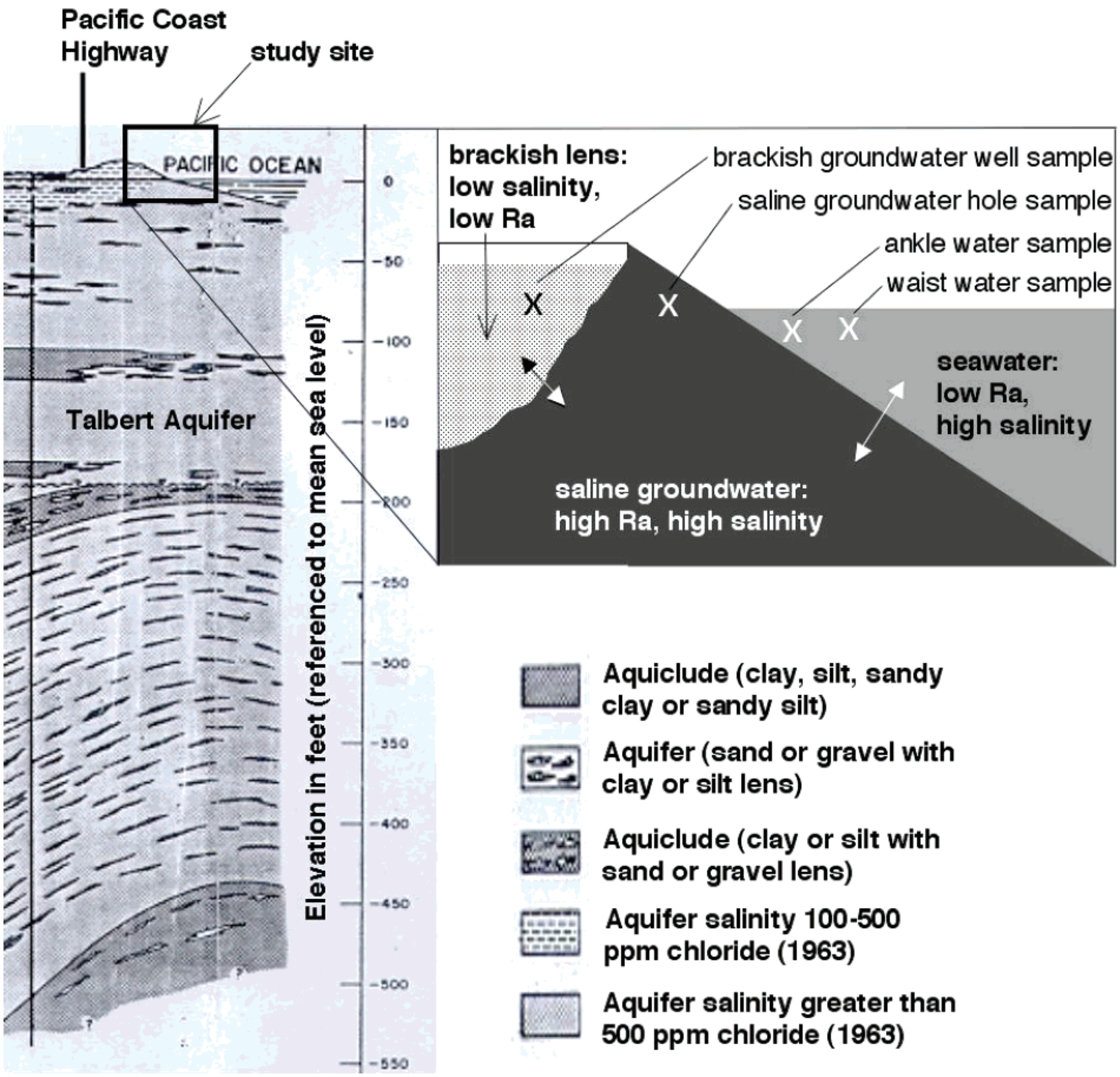

FIGURE 2. Schematic of the hydrogeology of the study site, courtesy of the Orange County Water District, Fountain Valley, CA. A drawing of our study area is shown at the right illustrating the hypothesized exchange between unconfined aquifers and the surf zone at Huntington Beach, CA. X's show locations within the surf zone and the surficial aquifers where samples were collected.

November (*17*), a brackish water lens (salinity range 3−9 ppt) exists during the summer as little as 3 m below the beach surface and may extend to within 20 m of mean low water (MLW). Each of the three water masses highlighted in the inset of the figure possesses unique chemical characteristics that enable their tracking. The combination of salinity and naturally occurring radium isotope activities allow differentiation between brackish groundwater, saline groundwater (SGW), and seawater (*18*−*20*). Radium in groundwater originates from the decay of uranium and thorium isotopes in the soil/bedrock matrix. In the presence of high ionic strength solutions, radium cations readily desorb via ion exchange (*21*,*22*); complete radium desorption has been observed from sediments greater than 128 μm in diameter (such as sand) near 13 ppt (*23*). Radium isotopes have been used to document groundwater discharge and its impact on nutrient cycling in several relatively wet coastal regions of the country, including the Carolinas, Florida, and New England (*24*−*26*). No published studies have utilized radium isotopes to explore the association of groundwater with bacterial contamination at any site, and few studies have used Ra isotopes to study groundwater discharge in a wave-dominated sandy beach along the semi-arid west coast (*27*).

In the present study, we establish the exchange of SGW between the surficial, unconfined aquifer and the surf zone, ascertain the flux of SGW, and determine the associated nutrient loads to the surf zone from this source using short-lived radium isotopes ^{223}Ra and ^{224}Ra (half-lives of 11.4 and 3.7 d, respectively). Given this mechanism of exchange between the subsurface waters and the surf zone, we show that the temporal variability of FIB is consistent with that of radium and nutrients, pointing to a possible connection between groundwater discharge and microbial pollution at Huntington Beach.

Materials and Methods

Field Sampling. ***Surf Zone.*** Four 3-d sampling excursions were conducted during the summer of 2003 during two neap tides and two spring tides (studies A−D, Table 1). Two low tides and two high tides were sampled for a total of four sampling events during the majority of the sampling excursions. During each event, seawater was collected from the

TABLE 1. Dates and Tidal Conditions during the Five Field Outings[a]

study	dates	sampling	spring or neap (tide range)
A	Aug 2−4, 2003	SZ/cross shore	neap (0.7 m)
B	Aug 9−11, 2003	SZ/cross shore	spring (1.2 m)
C	Aug 16−18, 2003	SZ/alongshore	neap (0.6 m)
D	Aug 26−28, 2003	SZ/alongshore	spring (1.1 m)
E	Sept 10−12, 2003	brackish water lens	spring (1.0 m)

[a] SZ is surf zone.

near surface of the surf zone at ankle and waist depth at lifeguard stations 9 (33°38′327″ N, 117°58′577″ W) and 10 (33°38′416″ N, 117°58′725″ W), which are located at the center of the beach pollution problem (see Figures 1 and 2) (*4*). In addition, at each low tide, a SGW sample was obtained by pumping groundwater from the surficial unconfined aquifer from a shallow hole (<1 m deep) in the intertidal zone, far enough from the swash zone so that no surface water contaminated the hole. Samples were analyzed for ^{223}Ra and ^{224}Ra activities, FIB, salinity, temperature, and nutrients as described below.

Other Locations. To gain an understanding of the cross-shore and alongshore spatial variability in water characteristics, we obtained (i) seawater samples from approximately 500, 1000, and 1500 m offshore of station 9 during a neap and spring tide (studies A and B) and (ii) groundwater from shallow holes (<1 m deep) dug in the intertidal zone and seawater from knee depth in the surf zone at stations 7−11 (Figures 1 and 2) during low tide under spring and neap tide conditions (studies C and D).

To characterize other potential local water sources to the surf zone, we collected samples during spring and neap tidal conditions at the mouths of the Santa Ana River and Talbert Marsh when the tide was ebbing (studies A and B) and groundwater from the Talbert Aquifer, a confined aquifer managed by the Orange County Water District (OCWD). The aquifer sample was collected from a well (well M31, OCWD) screened between 25 and 50 m, 500 m from the ocean (Figure 1).

Samples from the brackish surficial aquifer were collected using screened PVC well points. These were installed using a hand auger at stations 8−10 approximately 50 m from MLW (study E). Screens were positioned approximately 3 m below the surface of the sand, within the upper surficial aquifer. A total of four 76 L large volume groundwater samples were pumped from each well during two low tides and two high tides, starting 12 h after well-point installation. Prior to pumping water samples, wells were purged for 5 min. All samples obtained during these studies were analyzed for ^{223}Ra and ^{224}Ra activities, FIB, salinity, temperature, and nutrient concentrations as described below.

Water Analyses. *Radium Isotopes.* Ninety-five and 38 L of water were collected for surface and groundwater samples, respectively, unless otherwise noted. Water was passed over manganese-impregnated acrylic fibers (*28*) at a flow rate less than or equal to 1.5 L/min in the field immediately after collection. Plugs of untreated acrylic fiber were placed in the column to reduce the deposit of sediment and plankton from the sample on the impregnated acrylic fibers. Within at most 3 d after water collection, short-lived Ra isotope activities (^{223}Ra and ^{224}Ra) were measured with a scintillation cell interfaced to a photomultiplier and a delayed coincidence counter (*29*). The analytical error associated with this measurement technique is approximately 10% (*30*). A preliminary study at Huntington Beach during June 2003 showed that the correction for ^{228}Th-supported ^{224}Ra activity was at most 5% and on average 3% ($n = 12$) (see Supporting Information for more details). This finding is in agreement with Rama et al. (*30*), who assert that because of its particle reactivity, ^{228}Th-supported ^{224}Ra activity is usually insignificant in nearshore waters. Given the low corrections, especially relative to our analytical errors, we did not run further ^{228}Th corrections. Because results presented here are based on activity differences between groundwater and coastal samples, not including this small correction will not influence the gradients observed in this work (e.g., our ^{224}Ra activity data for all samples is systematically about 3% too high).

FIB. Fifty milliliters of each large-volume sample were collected in a sterile container, immediately stored on ice, and transported to the lab for FIB analyses. TC, EC, and ENT were quantified from 10 mL of water diluted with 90 mL of Butterfield buffer (Weber Scientific, Hamilton, NJ) using Colilert-18 and Enterolert (IDEXX, Westbrook, ME). Tests were implemented in a 97-well format following the manufacturer's directions within 6 h of water collection and allowed detection of organisms between 10 and 24 192 most probable number (MPN)/100 mL.

Nutrients. Thirty milliliters of 0.2 μm filtered water were subsampled from the large-volume samples, immediately stored on ice, and then frozen. Samples were analyzed for dissolved nitrate, ammonium, silica, and ortho-phosphate using an AlpChem autoanalyzer and standard methods.

Salinity and Temperature. Salinity and temperature of large water samples were measured in the field using a probe (YSI model 30, Yellow Springs, OH). To obtain a more precise estimate of salinity, 10 mL of water was subsampled from the large-volume samples, filtered through a 0.2 μm filter, and stored on ice for densiometric analysis (Anton-Paar model GmbH, Graz, Austria). Densities were converted to salinities with the UNESCO Equation of State (IES 80) (http://fermi.jhuapl.edu/denscalc.html as described in ref *28*).

Flux Calculations. A simple mass-balance model was applied to a box defined by the shoreline between stations 9 and 10 (280 m apart) and the offshore edge of the surf zone (approximately 20 m from the shoreline) to encompass the width of the surf zone. The amount of groundwater needed to supply the excess radium activity observed in the box (average surf zone radium activity minus offshore seawater activity) was determined by performing a mass-balance for each sampling event. The radium activity in the box was designated by averaging all measurements made within the box (stations 9 and 10, both ankle and waist measurements, typically $n = 4$) during a given sampling event. Although surf zone radium activity measurements did not extend past 10 m in the offshore direction, we assumed the surf zone was well-mixed (*5*), so that the calculated average radium activity applied to the entire 20 m wide surf zone box. The offshore sample with the lowest radium activity was chosen as the seawater end member, while the SGW sampled from the shallow hole in the intertidal zone at low tide closest in time to the surf zone samples was chosen as the groundwater end member. Because the residence time of water in the surf zone is much shorter than the half-lives of the radium isotopes, we considered the short-lived Ra isotopes conservative tracers within the surf zone. We also assumed that the time scale of exchange between saline aquifer and the surf zone is fast relative to the isotope decay time scale. This later assumption is reasonable because the shallow holes from which we sampled SGW are consistently covered with seawater during high tide, facilitating rapid exchange (*39*). These assumptions will be revisited in the Results and Discussion section, where we compare fluxes calculated with both ^{223}Ra and ^{224}Ra. If decay is important, then flux estimates should vary considerably between those calculated with ^{223}Ra and ^{224}Ra.

Moore (*24*) suggested an equation to calculate the groundwater discharge needed to balance the excess radium observed in a coastal environment. This equation can be adapted to the Huntington Beach field site to calculate a groundwater seepage rate per unit length of shoreline as follows

$$F_{\mathrm{sgw}} = \frac{(A_{\mathrm{box}} - A_{\mathrm{offshore}})V_{\mathrm{box}}}{A_{\mathrm{sgw}}L\tau} \quad (1)$$

where F_{sgw} is the saline groundwater flux in units of volume per time per unit length of beach, τ is the residence time of water in the box, L is the length of the shoreline of the box, and A_{box}, $A_{offshore}$, and A_{SGW} are the activities of radium in the box, offshore, and in SGW, respectively. The accompanying flux of nutrients is calculated as follows

$$F_{\mathrm{nut}} = C_{\mathrm{nut}}F_{\mathrm{sgw}} \quad (2)$$

where C_{nut} represents the concentration of the nutrient of interest in SGW.

The concentration of FIB in SGW, necessary to account for a specific FIB level in the surf zone (if indeed SGW is an FIB carrier), can be estimated using the following equation

$$C_{\mathrm{FIBSGW}} = C_{\mathrm{FIBSZ}}\, f^{-1} \quad (3a)$$

where C_{FIBSZ} is the concentration of FIB in the surf zone and f is the fraction of water in the surf zone that is SGW as determined by radium activities

$$f = \frac{V_{\mathrm{sgw}}}{V_{\mathrm{box}}} = \frac{A_{\mathrm{box}} - A_{\mathrm{off}}}{A_{\mathrm{sgw}} - A_{\mathrm{off}}} \quad (3b)$$

where V_{sgw} is the volume of water in the box that is SGW, and the remaining variables have been previously defined. In eqs 3a and 3b, it is assumed that all SGW discharged to the surf zone has a uniform FIB concentration.

Column Experiment. To ascertain the importance of filtration on FIB transport in the subsurface of Huntington Beach, we conducted filtration experiments such as those described by Zhuang and Jin (*32*). Sand and SGW were collected concurrently from the surficial aquifer at Huntington Beach near station 9 and chilled at 4 °C for 2 d. Sand was packed into a 3.5 cm diameter 10 cm long glass chromatography column using a wet packing method to reduce air spaces. SGW was seeded with ENT-rich bird feces collected at the field site so that the final concentration of ENT was 81 700 MPN/100 mL. ENT was chosen for the experiment as this organism has been responsible for the majority of beach closures at this site (*4*). The ENT-rich SGW was pumped through the column at a flow rate of approximately 0.5 mL/min for approximately 20 h. After 15 pore volumes of ENT-rich feed were passed through the sand, the feed was changed to ENT-free SGW. Fractions of 7.5 mL were collected throughout the experiment using an automated fraction collector. The flow rate was chosen based on flow rates used by other researchers in similar column experiments (*32*) and was not chosen to mimic actual subsurface flow rates at our field site. The experiment was conducted at 25 °C in a laminar flow hood under low light conditions. Fractions were analyzed for ENT within 6 h of collection using membrane filtration on m-Enterococcus agar (Remel, Lenexa, KS) following standard methods (*33*). A flask containing 1 L of SGW with an identical amount of bird feces was monitored alongside the column experiment to quantify any die-off or growth of ENT in the feed during the 24 h experiment.

Results and Discussion

Marine Observations. Climatic and oceanographic conditions were similar throughout our field project (studies A−E) with the exception of water temperature. The sea surface temperature was 18−20 °C (typical for this season) on all occasions with the exception of sampling excursions A (neap tide) and D (spring tide), when water temperatures fell to 15 °C. In both cases, cooling events were accompanied by a bloom of autofluorescing plankton that caused increased turbidity in surface waters. The temporal and spatial scales of the cooling events are consistent with a synoptic upwelling event (*34*). Waves were generally out of the south to south−southwest with wave faces measuring 0.5−1.5 m generating upcoast (northerly) littoral drift within the surf zone. On average, the surf zone was approximately 20 m wide. During high tides, the majority of waves broke directly on the beach face, while at low tides most wave energy was dissipated on a sand bar located approximately 10 m from mean low tide. On the basis of the Longuett−Higgens equation for wave-driven littoral drift (*35*), alongshore velocities were approximately 0.015 m/s when waves broke perpendicular to the shore when originating from the south−southwest and 0.5 m/s when waves emanated from the south and approached the shoreline at a more oblique angle (*36*). Rip cells were approximately 200−300 m in length, and based on a study by Boehm (*36*), water introduced to the surf zone is ejected, on average, after traversing one rip cell when waves are from the south−southwest or about 10−12 rip cells when waves are from the south. On the basis of these estimates of littoral drift, rip cell spacing, and dilution length scales, we approximate that the residence time of water in a rip cell ranged from 1 to 4 h during the four studies when water was sampled in the surf zone (studies A−D). These time scales will be used to calculate groundwater flux.

Exchange between the Subsurface and the Surf Zone. *Radium*. Elevated ^{224}Ra and ^{223}Ra activities were detected in all surf zone samples, average activities of 29.6 (^{224}Ra) and 0.97 (^{223}Ra) dpm/100 L compared to 11.8 and 0.46 dpm/100 L, respectively, 1500 m offshore from the surf zone ($n = 2$). This observed distribution of radium activities is consistent with a coastal groundwater source (Figure 3A shows ^{224}Ra distribution, see Supporting Information for similar distribution of ^{223}Ra) (*22*). SGW from the unconfined beach aquifer had activities nearly 20 times greater than that of the surf zone waters (average ^{224}Ra = 472 dpm/100 L and ^{223}Ra = 20.0 dpm/100 L). Activities in ebb flow in the Santa Ana River water were similar to those of the surf zone (^{224}Ra = 34.1 dpm/100 L, ^{223}Ra = 1.76 dpm/100 L ($n = 2$)). Talbert Marsh (TM) ebb flow was elevated in Ra relative to the surf zone, but still about 4-fold lower than SGW (TM: ^{224}Ra = 121 dpm/100 L, ^{223}Ra = 4.22 dpm/100 L ($n = 2$)). The Talbert Aquifer was extremely high in radium based on one measurement (Figure 3B). On the basis of the local geology (*38*), the Talbert Aquifer might communicate with the surficial aquifer at the beach (Figure 2). The brackish water lens samples (salinity less than 10) were not as elevated in Ra as SGW likely due to the tendency for radium cations to remain sediment-bound in solutions of ionic strength less that 13 ppt (*23*). ^{223}Ra and ^{224}Ra activities for all samples collected are shown in Figure 3B.

On the basis of the presented measurements, it is likely that radium activities observed in the surf zone are primarily due to the mixing of high radium SGW from the unconfined beach aquifer with low radium offshore waters. Specifically (i) radium is consistently elevated in the SGW which directly communicates with seawater and (ii) the closest surface water with Ra activities higher than the surf zone is the Talbert Marsh 1800 m to the south, and this source would be diluted by at least 50% as it first enters the surf zone (*5*) and then diluted even more by rip currents as it is advected north (*36*, *37*). This conclusion is further corroborated by the lack of alongshore differences in surf zone radium levels (Figure 3A), as would be expected from a Talbert Marsh source diluted

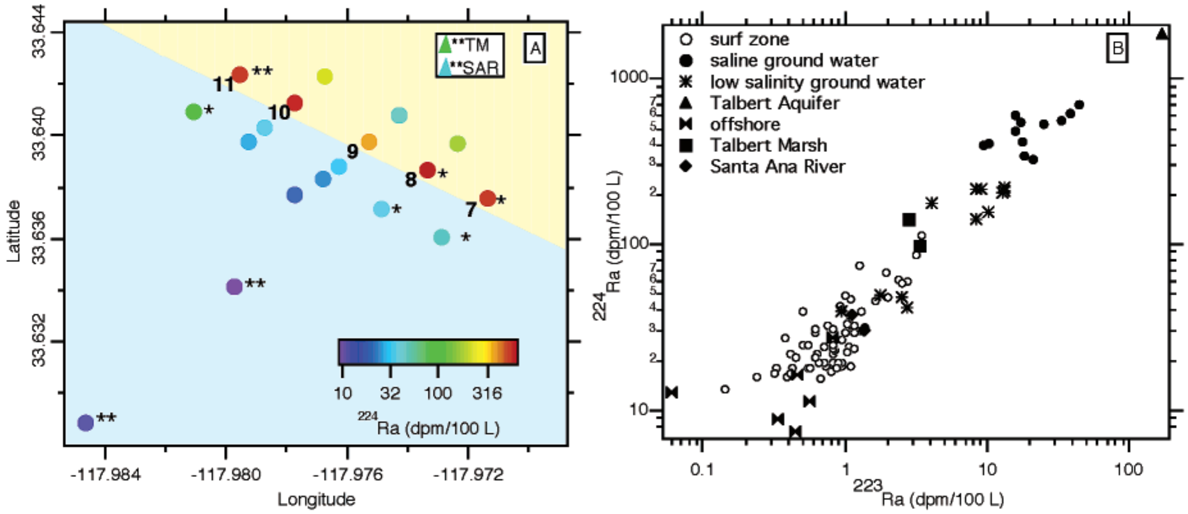

FIGURE 3. (A) Average ^{224}Ra activities at each station. Color is proportional to the log of the ^{224}Ra level. Levels determined by one and two measurements alone are denoted by a single asterisk or double asterisks, respectively. The Talbert Marsh (TM) and the Santa Ana River (SAR) ^{224}Ra activities are shown as triangles but are not positioned at the actual sample location. (B) ^{224}Ra verses ^{223}Ra for each measurement collected. Classification of water is denoted by symbols. A diagram similar to 3A for ^{223}Ra can be found in the Supporting Information.

TABLE 2. Averages and Standard Deviations of Nutrients in Various Waters

water type (no. of observations)	NH_4^+ (μM)	ortho-P (μM)	SiO_4 (μM)	NO_3 (μM)	total inorganic N (μM)	oxygen status
surf zone ($n = 58$)	0.69 ± 0.47	0.08 ± 0.06	5.65 ± 3.61	0.63 ± 0.37	1.32 ± 0.62	oxic
saline GW ($n = 12$)	4.05 ± 2.89	0.49 ± 0.34	13.0 ± 8.64	7.46 ± 6.87	11.5 ± 7.65	oxic
brackish lens ($n = 17$)	2.15 ± 1.06	1.12 ± 0.45	28.8 ± 5.58	341 ± 152	343 ± 153	suboxic (2-3 mg/L)
Talbert Aquifer ($n = 1$)	1140	0.06	54.8	0.10	1140	anoxic
1500 m offshore ($n = 2$)	0.70 ± 0.19	0.05 ± 0.04	2.75 ± 0.77	0.30 ± 0.08	1.00 ± 0.27	oxic
SAR ($n = 2$)	1.72 ± 0.16	0.10 ± 0.03	9.67 ± 5.24	0.73 ± 0.22	2.45 ± 0.07	oxic
TM ($n = 2$)	1.01 ± 0.99	0.10 ± 0.03	4.17 ± 2.12	0.85 ± 0.16	1.85 ± 1.15	oxic

by rip currents and mixed during alongshore transport within the surf zone (conservatively assuming radium decay is not important) (*36*, *37*).

Nutrients. Average nutrient concentrations and approximate redox status from the surf zone, ebb flow from the river and marsh, SGW, the brackish water lens, Talbert Aquifer, and open seawater (station furthest offshore) are given in Table 2. Nitrate and silica concentrations in the surf zone are significantly elevated (factor of 2) when compared to offshore waters. The Talbert Aquifer, which is anoxic, is high in ammonium. Nutrient concentrations are highly elevated in the groundwater samples relative to the surf zone both in the saline surficial aquifer and the brackish water lens.

The brackish water lens was especially elevated in nitrate relative to other waters (average = 341 μM). The highest nitrate levels were observed in the samples taken with the well point from station 8 (average = 507 ± 52 μM ($n = 4$)), and the lowest levels sampled in the brackish water lens were at station 10 (166 ± 27 μM ($n = 4$)). Water levels fluctuated in the wells with the changing tide, and wells contained water with higher salinity during high tides compared to low pointing to a hydrologic connection between the sea and the brackish lens. The high nitrate levels in this water were documented previously in a report by Komex H_2O Science (*37*). They installed additional wells south of station 8, closer to the mouth of the Talbert Marsh, and found lower nitrate levels (40−145 μM). Our findings together with those reported by Komex suggest that high nitrate may be unique to the brackish groundwater near the stretch of beach between stations 8 and 10.

Coefficients of determination (COD) (Matlab, Mathworks, Natick, MA) between ^{224}Ra activities and ammonium, orthophosphate, and silica in the surf zone reveal that ^{224}Ra accounts for 23%, 30%, and 15% of their variance ($p < 0.05$), respectively, supporting the idea that these nutrients are associated with groundwater inputs. COD for ^{223}Ra and these nutrients were similar. While nitrate is higher in groundwater relative to surface waters, we did not find that it covaried significantly with radium activities in the surf zone.

Mixing. Mixing diagrams were constructed by plotting ^{224}Ra and total inorganic N as functions of salinity using data from all samples (Figure 4A and B). Mixing lines appear curved because of the log−linear presentation of the data. End members representing seawater, SGW, and brackish groundwater were chosen as samples with an oceanic salinity and the lowest radium activity, oceanic salinity and the highest radium activity, and the lowest salinity, respectively. Because we obtained only one sample from the Talbert Aquifer, it alone was chosen as that aquifer's end member in Figure 4B.

On the basis of the ^{224}Ra−salinity mixing curves in Figure 4A, samples collected in the surf zone and the surficial unconfined saline aquifer are mixtures of the seawater and SGW end members. Water collected from the brackish lens may represent a mixture of an unknown freshwater end member and SGW. However, radium desorption is a function of salinity (*23*), so radium does not behave conservatively along the salinity gradient between these two aquifers. The ^{224}Ra in the brackish groundwater is higher than what would be expected from mixing between SGW and brackish groundwater end member based on the fact that the data fall above the mixing curve. This may signify that the region between these aquifers is one of radium desorption because of the changing salinity regime. One should note that in this discussion of mixing we assumed that decay of the isotopes

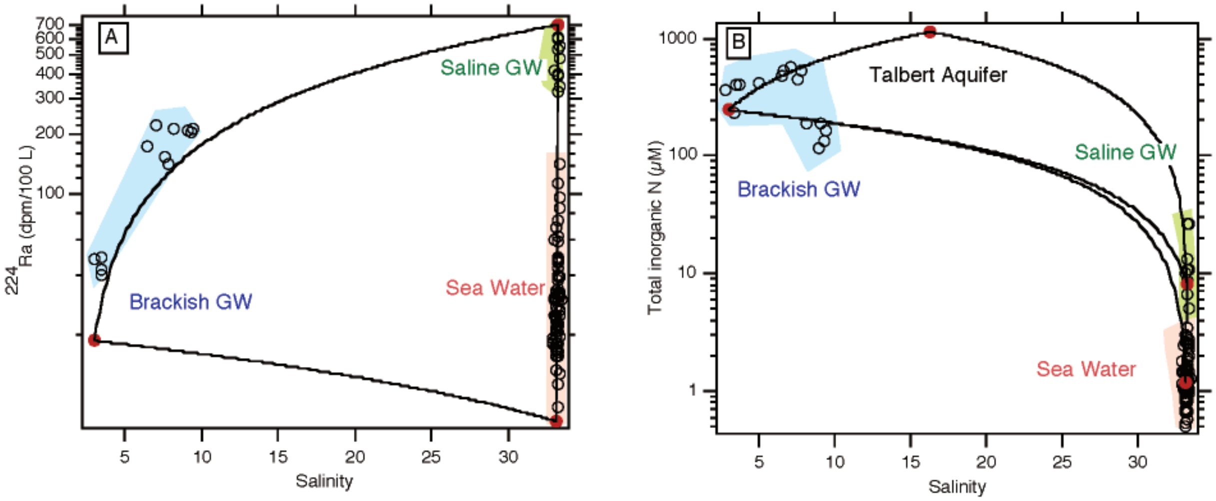

FIGURE 4. Mixing diagrams. End members are designated by red bullets. GW denotes groundwater. (A) ^{224}Ra vs salinity. (B) Total inorganic N vs salinity.

is small relative to the time scales of mixing. While we are fairly confident that this is true for mixing between SGW and the surf zone, we know less about mixing time scales between the brackish aquifer and the other sources. Exchange between the Talbert Aquifer and other end members is not illustrated as we are not certain of its hydrologic connection between other end members and how time scales of transport compare to radium decay. This may be investigated in a future study using long-lived ^{226}Ra and ^{228}Ra.

The total inorganic nitrogen–salinity mixing diagram (Figure 4B) also indicates that the surf zone water is predominantly a mixture of the SGW and seawater end members. This diagram may present a better illustration of interactions between the brackish water lens and other waters. The brackish water lens could represent mixing of either nitrogen-rich brackish groundwater and low-nitrogen SGW or seawater, or mixing of brackish groundwater and even higher nitrogen, intermediate salinity water, like that of the Talbert Aquifer. An additional possibility that is not illustrated in the mixing diagram is that the brackish water lens contains fresh runoff water that has infiltrated the subsurface which is rich in nitrogen from fertilizers or another nitrogen-rich source like sewage. It should be noted that the salinity gradient between the SGW and brackish aquifer is also accompanied at least occasionally by an oxygen gradient, and this could possibly exert some control over nutrient exchange and speciation within the groundwaters.

Groundwater and Nutrient Fluxes. Groundwater and nutrient fluxes were estimated using eqs 1 and 2 assuming the surf zone water residence times (τ) of both 1 and 4 h discussed previously. These estimates for τ, and the fluxes we calculate using them, should be viewed as first-order approximations.

On the basis of ^{224}Ra and ^{223}Ra activities in the surf zone and oceanic and saline groundwater end member activities, eq 1 predicts that the flux of SGW to the surf zone is influenced by tide level with approximately twice the groundwater flux during low tides compared to high (Table 3). During low tides, approximately 3.1–16 L/min of SGW per meter of shoreline is discharged to the surf zone, while during high tides, between 1.1 and 8.6 L/min/m is discharged. The range reported represents values obtained when assuming 4 and 1 h residence times, respectively and includes values acquired using both short-lived isotopes. Depending on the tidal condition, the fluxes calculated with the ^{224}Ra where 15% less, the same, or 30% greater than those calculated with ^{223}Ra. If decay were important within the time period of exchange between the SGW aquifer and the surf zone, then

TABLE 3. Flux of Saline Groundwater (SGW), Total Inorganic N ($NO_3^- + NH_4^+$), Ortho-Phosphate, and Silica to the Surf Zone[a]

tide condition and residence time	SGW (L min^{-1} m^{-1})	total inorg N (μmol min^{-1} m^{-1})	PO_4^{3-} (μmol min^{-1} m^{-1})	SiO_4 flux (μmol min^{-1} m^{-1})
neap-high				
1 h	7.3 (8.6)	49 (58)	2.3 (2.7)	42 (50)
4 h	1.8 (2.1)	12 (16)	0.63 (0.67)	11 (12)
neap-low				
1 h	13 (12)	87 (84)	4.0 (3.8)	75 (72)
4 h	3.2 (3.1)	22 (23)	1.0 (0.96)	19 (19)
spring-high				
1 h	6.1 (4.6)	77 (58)	3.6 (2.7)	100 (76)
4 h	1.5 (1.1)	19 (15)	1.0 (0.67)	25 (20)
spring-low				
1 h	16 (12)	202 (155)	9.4 (7.2)	260 (204)
4 h	4.0 (3.1)	51 (39)	2.3 (1.8)	66 (51)

[a] Values predicted from ^{224}Ra appear first in each cell. Values predicted from ^{223}Ra appear in parentheses. Fluxes are per length of shoreline.

discharged SGW would have a lower radium signature than that measured in the shallow holes, with ^{224}Ra being more depleted than ^{223}Ra given its shorter half-life. If this were the case, then the fluxes predicted estimated by ^{224}Ra activities would be consistently smaller than those predicted by ^{223}Ra (eq 1). This is not observed in the data, supporting the idea that decay is not exerting a major control over the mass balance of these isotopes. It must be noted that the estimated fluxes are not those of pure terrestrial-derived groundwater but rather of a combination of all water that has been in contact with the aquifer rocks and soil and may predominantly be tidally pumped recirculated seawater as described in Moore (*40*). Future work will apply the model of Li et al. (*41*) to estimate contributions of terrestrial-derived water and tidally pumped and wave-setup-induced seawater circulation to these fluxes.

Estimates of groundwater contributions of inorganic nitrogen, ortho-phosphate, and silica to the surf zone follow from eq 2. As with groundwater flux estimates, these depend on tide stage and the residence time of water in a rip cell. Using the longer residence time (4 h) and SGW flux calculated using ^{224}Ra, groundwater is estimated to bring up to 51 μmol min^{-1} m^{-1} total inorganic N ($NO_3^- + NH_4^+$), 2.3 μmol min^{-1} m^{-1} orthophosphate, and 66 μmol min^{-1} m^{-1} SiO_4 (based on spring, low-tide conditions). Estimates for other tidal condi-

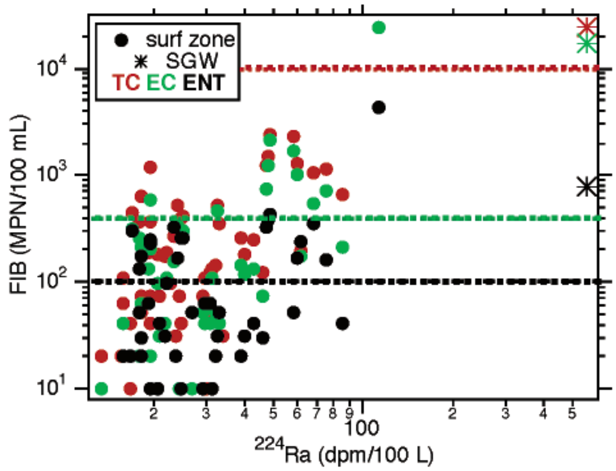

FIGURE 5. FIB verses ^{224}Ra for all surf zone samples (closed circles). FIB and ^{224}Ra results from the one SGW sample with elevated FIB are shown as large asterisks. The colored dashed lines represent the California single sample standards for the three FIB.

tions and using results for SGW discharge estimates with ^{223}Ra can be found in Table 3, with the following order of decreasing nutrient flux (except for silica): spring-low, neap-low, spring-high, neap-high. Nutrient fluxes estimated from activities of both ^{224}Ra and ^{223}Ra vary in the same proportions and share the same tidal variability as the estimates for SGW discharge.

Relationship between FIB and Groundwater Discharge. FIB were found in the surf zone as well as in the ebb flow of the river and marsh. Of the 62 surf zone samples collected, 1 TC, 10 EC, and 17 ENT measurements were in excess of the California single-sample contact standards. In most cases, values exceeding the standards occurred during spring tides (events B and D), as previously observed (*4*). Measurements at the river mouth were below the standards, but those at the outlet of the marsh were above standards for EC and ENT. One SGW sample collected at station 9 contained FIB in excess of the single-sample standard for all FIB (>24 192 (TC), 17 329 (EC), and 776 (ENT) MPN/100 mL). Other saline groundwater samples contained lower levels of TC, EC, and ENT (typically less than 60 MPN/100 mL). Samples from the brackish lens and Talbert Aquifer were all negative for FIB.

Correlations between $\log_{10}$ FIB values of surf zone measurements and other chemical parameters exist as indicated by variance analysis (Matlab, Mathworks, Natick, MA). ^{224}Ra accounts for 36%, 38%, and 24% of the variance in log TC, log EC, and log ENT ($p < 0.05$) with similar results for ^{223}Ra. Positive, significant correlations exist for all three FIB and NH_4^+ and PO_4^{3-} with each nutrient accounting for 12−20% of the log FIB variability. A closer examination of ^{224}Ra and FIB levels shows that high FIB values are frequently accompanied by high Ra activities (Figure 5, see Supporting Information for accompanying ^{223}Ra graph). FIB levels are likely to be elevated when ^{224}Ra activities are greater than 30 dpm/100 L. The results are suggestive of a link between groundwater discharge and FIB levels in the surf zone and support the hypotheses that either nutrients or other constituents such as dissolved organic matter from groundwater influence the persistence/growth of FIB in the surf zone (*16*) or groundwater itself is a source of FIB.

We found significant (based on a nonparametric Kruskal−Wallis test (Matlab, Mathworks, Natick, MA)), spring-neap tidal variations in ^{224}Ra ($p < 0.05$) and ^{223}Ra ($p < 0.1$) in the surf zone that match tidal variations in FIB ($p < 0.05$), ammonium ($p < 0.05$), silica ($p < 0.05$), and phosphate ($p < 0.05$) with these constituents significantly higher during spring tides compared to neap (Figure 6A). During all three spring tide sampling events, the beach between stations 9 and 10 or just south of 9 were posted by the Orange County Health Care Agency as unfit for swimming based on elevated levels of FIB. During low tide, radium and ammonium levels in the surf zone were elevated compared to high tide (Figure 6B, $p < 0.05$). FIB were not significantly different between these two tidal conditions without considering the fortnightly tidal condition. When the differences between FIB during high and low tides are considered for spring tides alone, we find significantly higher levels of TC and EC during low tides compared to high ($p < 0.05$), although differences between ENT are still insignificant. Further, the highest levels of all three FIB were documented during a spring low tide.

Using eqs 3a and 3b, the concentration of FIB in SGW necessary to cause ENT levels of 104 MPN/100 mL in the surf zone (the California single-sample recreational contact standard) was calculated. Because the fraction of groundwater in the surf zone depends on tide level, so does the required ENT level. On the basis of both ^{223}Ra and ^{224}Ra activities, during spring, low tides ENT of 1500 MPN/100 mL in groundwater is required to achieve 104 MPN/100 mL in the surf zone (7% of the water in the surf zone box we sampled was of SGW origin based an average of predictions from both isotopes). Spring high tides represent the tidal condition during which the highest concentration of ENT in SGW (5200 MPN/100 mL) is needed to achieve 104 MPN/100 mL in the surf zone (approximately 2% of the water in the surf zone box was of SGW origin). The predicted values are much higher than the levels of ENT we observed in the surficial aquifer on all but one occasion. They are, however, on the order of values reported for nuisance runoff in the surrounding watershed (*42*) and lower than what would be expected in raw sewage (*43*). The fact that we did not consistently find ENT in excess of these levels in SGW samples does not necessarily disprove that FIB are transported into the surf zone through the subsurface from a FIB source. The subsurface is a complex environment, and the subsurface transport of bacteria in a plume is not fully understood (*44*). If a plume of FIB exists within the surficial aquifer, it likely does not extend spatially over the entire aquifer. Rather, it probably occupies a small spatial area contaminated with extraordinarily high FIB levels. Locating such a hot spot would require temporally and spatially intensive sampling using multidepth wells. The fact that we did encounter at least one SGW sample with very high FIB levels suggests that this scenario is perhaps possible.

Column Experiment. We conducted a simple column experiment to test whether subsurface transport of ENT through the porous sand matrix at Huntington Beach was possible. Over the course of the experiment, we did not observe a change in ENT in the control, suggesting no growth or die off of ENT in the source solution during the experiment.

Results from the column experiment (Figure 7) illustrate that ENT are not filtered significantly by the column and that complete breakthrough is observed within approximately 10 pore volumes. Near the end of the experiment, colonies on plates were just beyond our abilities to count and thus assigned the highest number of colonies countable (19 824). We estimate that 4.01×10^5 ENT were introduced into the column from the feed solution and 3.86×10^5 ENT were collected at the exit of the column over the course of the entire experiment. The introduction of nonseeded SGW from the field site at the end of the experiment appears to have caused a flush of ENT from the sand that were previously sorbed. On the basis of the close balance between introduced and collected ENT we achieved, it is surprising that ENT in collected fractions did not drop to 0 at the end of the experiment. There are several possible explanations for this including (i) ENT were present in the sand prior to seeding were flushed, (ii) ENT were growing within the column, (iii)

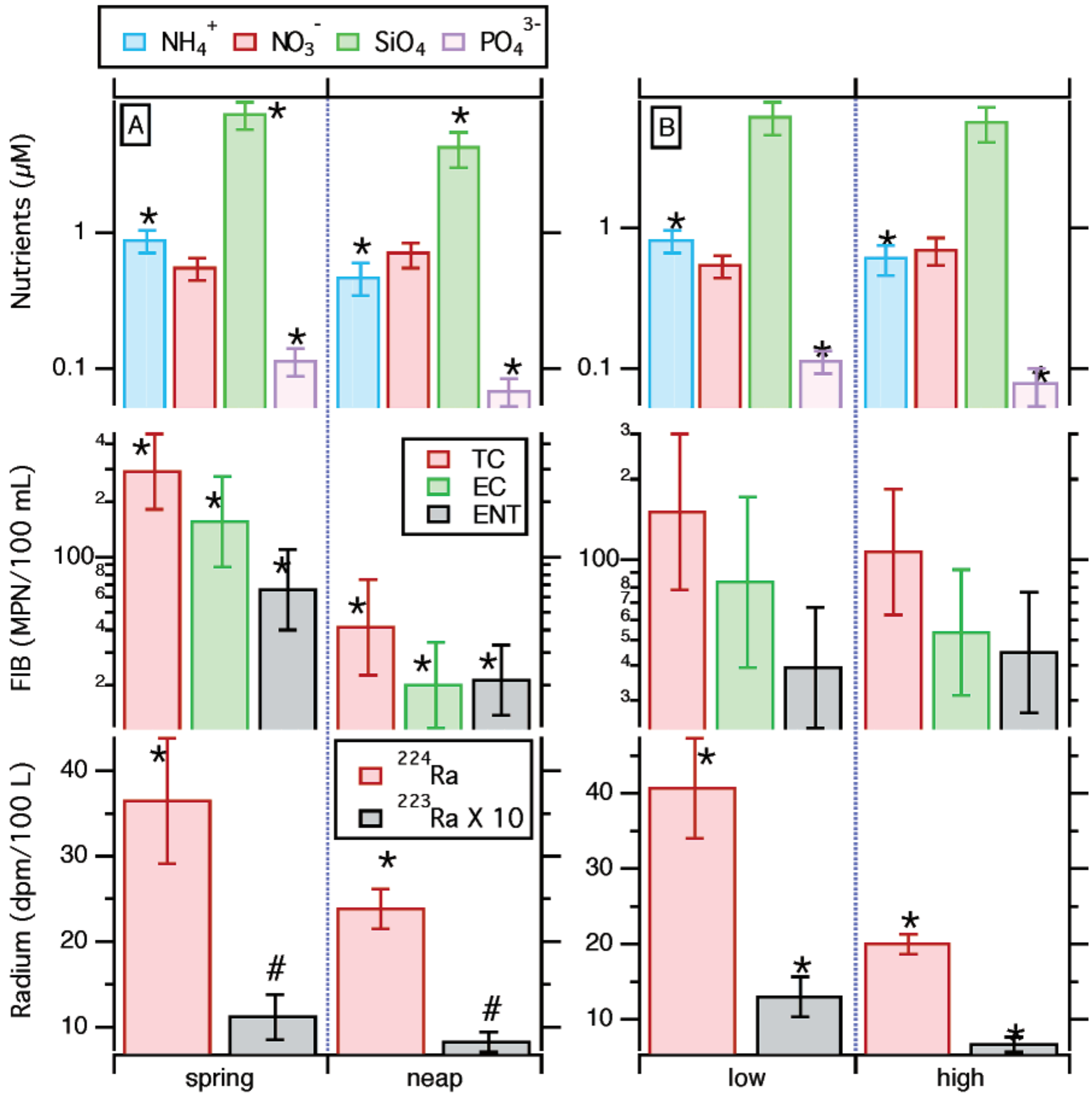

FIGURE 6. Comparison between radium, FIB, and nutrient levels at spring and neap tide (A) and at low and high tides (B). The bars show the average (radium and nutrients) or geometric mean (FIB) of surf zone samples collected under designated tidal condition. Error bars represent 95% confidence intervals. An asterisk denotes significance differences at 95% ($p < 0.05$), while # denotes significance at 90% ($p < 0.1$) between parameters in the two compared conditions.

we underestimated the concentration of ENT in the feed, (iv) or we overestimated ENT in the fractions. If the experiment were run for longer, we presumably would have observed a decline in ENT at the outlet of the column. More work will be done to understand the transport of ENT through this porous media and the implications for transport scales at the field site. Our results suggest that filtration does not effectively prevent the subsurface transport of ENT associated with SGW through the sand samples of Huntington Beach.

Synthesis. Because we did not find consistent extraordinarily high FIB in the surficial aquifer, we cannot assert that groundwater is a source of FIB. However, several findings indicate that this possibility should not be dismissed. (i) One SGW sample contained very high levels of FIB, relative to those observed in the surf zone (Figure 5, asterisks). (ii) Sand does not readily filter ENT from SGW. (iii) SGW ENT levels necessary to account for ENT equal to the California single-sample standard in the surf zone, based on the SGW discharge calculations, are relatively low compared to what is typically found in raw sewage and on the order of what is typical of nuisance runoff, both of which potentially could be a source of ENT to the subsurface. (iv) Short-lived radium isotopes covary with FIB over fortnightly, diurnal, and semi-diurnal tidal scales. Moreover, since SGW discharge appears to be a source of nutrients to the surf zone, discharged SGW could be providing an environment that allows increased persistence or possibly extraenteric growth of FIB, as suggested by Desmarais et al. (*16*) to occur in Florida sediments. The exact process by which FIB is delivered or enhanced as a result of SGW discharge needs to be further investigated. Short-lived radium isotopes may provide a valuable tool for quantifying the subsurface exchange of seawater and groundwater in FIB-impacted coastal environments and may be applied to other sites.

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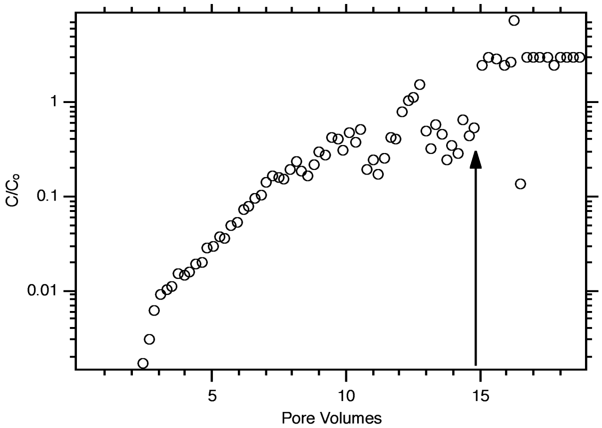

FIGURE 7. Results of column filtration experiments. Arrow indicates change in feed to unseeded SGW. C_0 represents the concentration of ENT in the ENT-rich feed: 2.67 × 10^4 MPN/100 mL.

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Supporting Information Available

Text and figures discussing ^{228}Th-supported ^{224}Ra corrections. This material is available free of charge via the Internet at http://pubs.acs.org.

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