

Temporal Evolution and Variability of Dissolved Inorganic Nitrogen in Beach Pore Water Revealed Using Radon Residence Times

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S Supporting Information

ABSTRACT: We coupled measurements of beach pore water residence time, determined using the radioisotopic tracer ^{222}Rn , with dissolved carbon and nitrogen chemistry to identify the temporal evolution and variability of dissolved inorganic nitrogen (DIN) concentrations in beach pore water along the Santa Barbara, California coastline. Pore water dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) ratios (DOC:TDN) were negative exponentially correlated with residence time. Mean pore water residence times were positively correlated with tidal amplitudes, and ranged from 4.4 to 6.4 days. We used this range in mean residence times to model radon residence time distributions (RTDs), and integrated them with modeled DIN vs residence time relationships (DIN-temporal evolution, or DIN-te curves) to derive volume-weighted mean (VWM) DIN concentrations. We observed 1.2-fold and 5.2-fold differences (20% and 420% increases) in VWM DIN concentrations over the range in modeled RTDs and DIN-te curves, respectively, and a maximum 6.4-fold difference (540% increase) in VWM DIN concentrations for an interactive shift in the RTD and the DIN-te curve. Our study suggests that accounting for temporal variability in the RTD and DIN concentration of pore water is necessary to obtain more accurate estimates of DIN delivery to coastal oceans.



INTRODUCTION

In coastal marine regions, dissolved inorganic nitrogen (DIN, the sum of ammonium, nitrite, and nitrate) can be a limiting nutrient for primary production^{1,2} but pollutant when supplied in excess, causing harmful algal blooms, eutrophication, and hypoxia.^{3,4} Sandy intertidal beaches can function as both sink and source of DIN to coastal oceans, moderating excess fresh groundwater DIN delivery from coastal aquifers due to land use impacts, and regenerating DIN from marine particulate and dissolved organic matter (POM and DOM) in seawater that is pumped through beach sands by waves and tides. This collective discharge of fresh groundwater and recirculating seawater to coastal oceans is termed submarine groundwater discharge (SGD).⁵ Recirculating seawater comprises a high percentage of SGD, even along coastlines with aquifer-ocean connectivity, ranging from 50% to over 99% of SGD.^{6–9} As a result, the regeneration of DIN from marine POM and DOM in recirculating seawater can be a dominant source of DIN delivered to coastal oceans via SGD,^{10–12} and is therefore an important process to understand when examining the role of beaches in coastal marine nitrogen cycles. However, characterizing this DIN delivery can be challenging due to high temporal variability in SGD and biogeochemical conditions in beach pore water (i.e., fresh groundwater and/or recirculating seawater within beach sands).

The temporal variability and hydrologic controls of SGD have been studied using direct measurements, numerical modeling, and radioisotopic tracers such as radon (^{222}Rn) and the radium quartet (^{223}Ra , ^{224}Ra , ^{226}Ra , and ^{228}Ra) (reviewed in ref 5). However, the temporal variability and biogeochemical controls on pore water DIN concentrations have received less attention, despite recognition of the dynamic biogeochemical conditions in pore water that can significantly alter DIN concentrations through time.^{11,12} One way to identify this temporal variability is to couple DIN concentration measurements with residence time determinations using a residence time tracer. Residence time is defined as the amount of time that has elapsed since a volume of groundwater (or pore water) entered the subsurface hydrologic system.¹³ Radon, a conservative, radioisotopic gas with a 3.8 day half-life, is continuously produced from the radioactive decay of ^{226}Ra adsorbed to sediments,¹⁴ and has been employed as a residence time tracer in terrestrial groundwater^{15,16} and beach pore water environments.¹⁷ Radon is able to resolve residence times up to ~15 to 19 days, making it an effective residence time tracer in beach pore water.¹⁷

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In this study, we demonstrate the first use of radon as a residence time tracer to identify the temporal evolution and variability of DIN concentrations in beach pore water. We coupled radon residence time determinations with measurements of DIN, total dissolved nitrogen (TDN), and dissolved organic carbon (DOC) in beach pore water at four predominantly marine-influenced beaches along the Santa Barbara, California coastline. Tides have been shown to exert a dominant control on pore water discharge^{6,18,19} and transit times,⁷ so we hypothesized that pore water residence time distributions (RTDs) would shift as a function of tidal amplitude. As such, integrating modeled RTDs with modeled DIN vs residence time relationships would allow a calculation of pore water volume-weighted mean (VWM) DIN concentrations, the variability of which could identify the interactive controls of temporal hydrologic and biogeochemical variability on DIN concentrations in beach pore water. SGD DIN delivery is routinely calculated assuming end-member concentrations that do not account for this variability. Our study (1) directly addresses the validity of this assumption, and (2) determines whether radon can be effectively employed as a residence time tracer to reveal patterns in the temporal evolution of DIN in beach pore water environments.

MATERIALS AND METHODS

Sites Description. The four study sites are located along the northern coast of the Santa Barbara Channel (Figure 1).

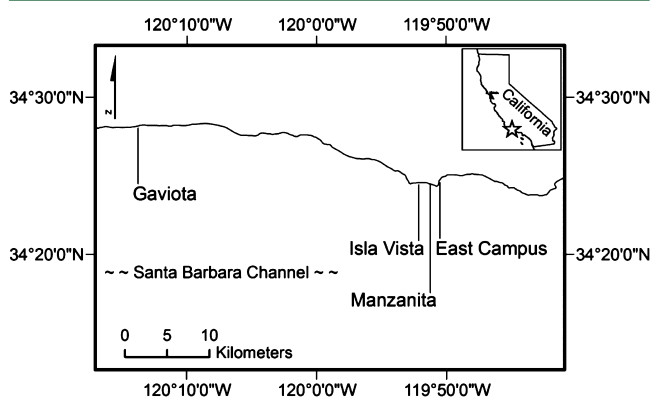


Figure 1. Study beach locations along the Santa Barbara, California coastline.

The coastal geomorphology of the region is characterized by unconsolidated sand beaches backed by 3–30 m high uplifted marine terraces.²⁰ Beach sediments consist of well-sorted fine to medium sands with an overall median grain size of 281 μm and a range of median grain sizes of 207–483 μm (J. Dugan, personal communication). Beach widths during the study period (July 2012 through June 2013), measured from the base of the bluff on the back beach to the water line, averaged 35 m and ranged from 10 to 55 m. Sand depths, measured from the sand surface to underlying bedrock, averaged 1.4 m and ranged from 0.4 to 2.3 m. Sand density and porosity were $1.4 \pm 0.1 \text{ g mL}^{-1}$ and 0.34 ± 0.02 (mean $\pm 1\sigma$; $n = 25$). Hydraulic conductivity, measured using the Hvorslev slug test method²¹ for two beach study sites, Manzanita and East Campus, was $0.6 \times 10^{-3} \text{ m s}^{-1}$ and $1.0 \times 10^{-3} \text{ m s}^{-1}$, respectively. The tidal regime in the Santa Barbara Channel is mixed semidiurnal and microtidal with tidal ranges less than 2 m.²²

Pore Water and Nearshore Seawater Sample Collection and Analysis. Pore water samples were collected during ebb tides for ammonium, nitrite + nitrate (hereafter nitrate), total dissolved nitrogen (TDN), dissolved organic carbon (DOC), particulate organic carbon and nitrogen (POC and PON, respectively), and salinity using hollow-core stainless steel piezometers (0.6 cm diameter, 2 cm screen length) and a hand-held peristaltic pump.²³ Ammonium, nitrate, TDN, and DOC samples were filtered with 0.7 μm GF/F filters (Whatman), POC and PON samples were collected on 25 mm 0.7 μm GF/F filters (Whatman), and salinity samples were unfiltered. Nearshore seawater samples were collected for the same analytes as pore water samples on the ebb to flood tide transition by wading in $\sim 1 \text{ m}$ water depth. Pore water samples were collected at multiple locations (distance between sample locations was $6.3 \pm 4.6 \text{ m}$; mean $\pm 1\sigma$) and at multiple depths ($0.7 \pm 0.4 \text{ m}$; mean $\pm 1\sigma$; range of 0.1 to 1.6 m), where feasible, along shore-normal transects running from the base of the bluff on the back beach to the wave run-up line.

Ammonium and nitrate concentrations were determined on a Lachat Flow Injection Autoanalyzer (Hach Company). The detection limit for ammonium and nitrate was 0.5 μM , precision was $\pm 0.4 \mu\text{M}$ for ammonium and $\pm 0.1 \mu\text{M}$ for nitrate, and accuracy was $\pm 6\%$ for ammonium and nitrate. DOC and TDN were measured by high temperature combustion (HTC) using a Shimadzu (Shimadzu) TOC-V_{CSH} system coupled with a Shimadzu Total Nitrogen analyzer.²⁴ The precision for DOC and TDN was ± 1 to 2 μM . Dissolved organic nitrogen (DON) was calculated as the difference between TDN and the sum of ammonium and nitrate. POC and PON were preacidified with HCl and measured by high-temperature combustion using a CE440 CHN elemental analyzer (Exeter Analytical). Specific electrical conductance values were measured using a YSI 3100 conductivity instrument (YSI) and were converted to salinity using a simplified general equation for salinity²⁵ originally described by Lewis.²⁶

Pore Water and Nearshore Seawater Radon Activity Sample Collection and Analysis. Pore water and nearshore seawater radon activity samples (Rn_{pw} and Rn_{sw} , respectively) were collected at two study beaches, East Campus and Manzanita, in 615 mL glass bottles (radon bottles) with custom gastight sampling caps. Rn_{pw} were collected by driving piezometers to target sampling depths and filling with approximately 250 mL pore water ($260 \pm 22 \text{ mL}$). Rn_{sw} were collected during the ebb to flood tide transition in $\sim 1 \text{ m}$ water depth by filling with approximately 500 mL of surf zone seawater ($452 \pm 65 \text{ mL}$). Rn_{pw} and Rn_{sw} were determined on a RAD7 Radon-in-Air instrument (DurrIDGE Company) using a closed-loop, continuous circulation with 15 min count intervals and total count durations of 1.25–3 h. The manufacturer quoted detection limit was 0.2 Bq L^{-1} (DurrIDGE Company).

Equilibrium Pore Water Radon Activity Incubations. Equilibrium radon activity samples (Rn_{eq}) were collected at distance intervals of $5.0 \pm 1.8 \text{ m}$ along the shore-normal transects at two study sites, East Campus and Manzanita, and at two depths where permissible, the top of the pore water table and at a depth equal to half the distance between the pore water table and sand surface. If sand at the sampling location was saturated, as occurred on the seepage face, then sand from only the top of the pore water table was sampled (i.e., at the surface). Approximately 50 mL of sand was collected and mixed in an approximate 1:4 to 1:5 volume ratio with unfiltered

Table 1. Nearshore Seawater Radon Activities ($n = 1$), Mean Pore Water and Equilibrium Radon Activities ($\pm 1\sigma$), and Mean Residence Times ($\pm 1\sigma$) for Manzanita and East Campus Study Beaches^{ab}

site	sample date	n	seawater ^{222}Rn	pore water ^{222}Rn	equilibrium ^{222}Rn ^c	mean τ (days)
Manzanita	12 Jul 2012	6	BD	3.6 ± 1.1	6.9 ± 2.7 (8)	4.4 ± 2.2
	30 Aug 2012	6	BD	4.1 ± 1.6	6.9 ± 2.7 (8)	6.4 ± 5.4
	27 Mar 2013	10	BD	3.3 ± 1.2	5.5 ± 0.8 (4)	5.6 ± 2.9
	26 Jun 2013	13	BD	3.2 ± 1.1	5.3 ± 0.9 (5)	5.8 ± 3.3
East Campus	17 Jul 2012	7	0.32	3.0 ± 1.3	4.7 ± 1.3 (8)	5.6 ± 3.6
	29 Aug 2012	11	BD	2.9 ± 0.7	4.7 ± 1.3 (8)	5.9 ± 2.3

^aAll ^{222}Rn activities in Bq L^{-1} . ^bBD = below detection limit. ^c(equilibrium ^{222}Rn sample n).

nearshore seawater in radon bottles. The sand-seawater mixture was initially purged for 20 min with ambient laboratory air to remove initial radon and incubated undisturbed (i.e., no shaking or agitation) in the laboratory for 2 weeks (16.6 ± 3.3 days) to allow ingrowth of radon. No temperature controls were implemented since fluctuations in water temperature were small; 21.5 ± 0.3 °C (mean $\pm 1\sigma$). At the end of the incubation period, equilibrium radon activities were determined using a closed-loop, continuous circulation on the RAD7 as described above. Equilibrium radon activity was calculated as

$$\text{Rn}_{\text{eq}} = \varphi(1 - \theta) \left(\frac{\text{Rn}_{\text{air}}V_{\text{air}} + \text{Rn}_{\text{pw}}V_{\text{pw}}}{M_{\text{sand}}\theta^{-1}} \right) \quad (1)$$

where Rn_{eq} = equilibrium radon activity (Bq L^{-1}), Rn_{air} = radon activity in the air loop (Bq L^{-1}), V_{air} = volume of the air loop ($1.5 \text{ L} + V_{\text{air}}$ of pore water sample bottle headspace), Rn_{pw} = pore water sample radon activity (Bq L^{-1}), V_{pw} = volume of pore water sample (L), M_{sand} = mass of sand (g), φ = sand density (g L^{-1}), and θ = porosity (dimensionless).

Radon Residence Time Calculations. Nearshore seawater is deficient in radon relative to pore water (Table 1). Once this seawater infiltrates into beach sands, becoming pore water, it begins to accumulate radon from the decay of ^{226}Ra , and will do so until the rate of radon production is equal to radon decay, yielding the equilibrium radon activity (Rn_{eq}). Pore water residence times can therefore be calculated using the disequilibrium between the pore water sample radon activity (Rn_{pw}) and mean equilibrium radon activity ($\overline{\text{Rn}}_{\text{eq}}$).^{16,17}

$$\tau = -\frac{1}{\lambda} \ln \left(1 - \frac{\text{Rn}_{\text{pw}}}{\overline{\text{Rn}}_{\text{eq}}} \right) \quad (2)$$

where τ = pore water sample residence time (days), λ = radon decay constant (0.18 days), Rn_{pw} = pore water sample radon activity (Bq L^{-1}), and $\overline{\text{Rn}}_{\text{eq}}$ = mean equilibrium radon activity (Bq L^{-1}). Nearshore seawater radon activities (Rn_{sw}) were subtracted from pore water radon sample activities, yielding pore water radon activities corrected for the initial seawater activity and nearshore seawater residence times of 0 days.

Residence Time Correction for Fresh Groundwater Radon Activity. Fresh groundwater mixing with recirculating seawater can inflate residence time estimates, since fresh groundwater typically has high radon activities relative to recirculating seawater,^{27,28} due to the high efficiency of ^{226}Ra adsorption to aquifer solids in low ionic strength waters.²⁹ The radon in fresh groundwater is primarily produced in the terrestrial aquifer, and therefore does not reflect radon production from beach sands. We used a two-component mixing model based on salinity measurements to calculate the

radon activity due solely to beach sand production for the 17 samples that contained fresh groundwater.

$$\text{Rn}_s = [\text{Rn}_{s+\text{gw}}(100) - \text{Rn}_{\text{gw}}P_{\text{sw}}]P_{\text{sw}}^{-1} \quad (3)$$

where Rn_s = pore water sample radon activity due to radon production in beach sands, $\text{Rn}_{s+\text{gw}}$ = pore water sample radon activity resulting from both beach sand and fresh groundwater aquifer production, Rn_{gw} = mean radon activity in fresh groundwater, and P_{sw} = percentage of seawater in pore water sample. The very low fresh groundwater discharge from bluff fractures did not allow us to sample and measure the fresh groundwater radon activity directly (i.e., Rn_{gw} in eq 3 above). Instead, we identified two nearby groundwater monitoring wells sited immediately adjacent to the coastal bluff geologic formations that backed our study beaches (i.e., marine terraces composed of sedimentary rocks; siltstones, mudstones, and shales). These two wells had measured radon activities of $5.1 \pm 0.5 \text{ Bq L}^{-1}$ and $10.1 \pm 0.7 \text{ Bq L}^{-1}$.³⁰ We used the higher radon activity of 10.1 Bq L^{-1} to represent Rn_{gw} , which is a maximal estimate since fresh groundwater radon that was produced in the coastal bluff aquifer decays exponentially with time once mixed with recirculating seawater in beach sands.

Residence Time Distribution (RTD) Modeling. A two-parameter gamma distribution was used to model the probability density distribution of pore water sample residence times:

$$h(\tau) = \frac{\tau^{\alpha-1}}{\beta^\alpha \Gamma(\alpha)} e^{-\tau/\beta} \quad (4)$$

where h = probability density of residence times (0–1), τ = residence time of pore water sample, α = shape parameter, β = $\tau_{\text{mean}}\alpha^{-1}$ (τ_{mean} = mean residence time), and $\Gamma(\alpha)$ = gamma function (a normalization constant making the area under the distribution equal to 1). A Kolmogorov–Smirnov test was used to assess the goodness of fit of the two-parameter gamma distribution to the pore water RTD.

RESULTS AND DISCUSSION

Fresh groundwater composed on average 0 to 15% of pore water for all study beaches (Supporting Information (SI) Table S1). Seventeen of 53 pore water samples for East Campus and Manzanita, where we collected radon samples for residence time determinations, contained $1.6 \pm 4.1\%$ (mean $\pm 1\sigma$) fresh groundwater. A minor fresh groundwater influence was similarly observed by Swarzenski and Izbecki in a SGD study of a nearby beach in Santa Barbara, with no net discharge of fresh groundwater during the dry summer, and brackish discharge only during infrequent rainstorms in winter when rainwater pooled and infiltrated the back beach sands.¹⁰

Sampled beach pore water radon activities ranged from 0.3 to 9.5 Bq L⁻¹ for wells sampled along a shore-normal transect for three sampling events conducted over the course of 1.5 years. Our mean pore water radon activities, ranging from 2.9 to 4.1 Bq L⁻¹, fall within the middle of their range of radon sample activities. For a well installed nearest to the waterline, the mean radon activity was 7.7 ± 1.0 Bq L⁻¹ (mean $\pm 1\sigma$). They did not measure equilibrium radon activities or residence times, but if we assume that their maximum pore water radon activity is representative of the equilibrium radon activity (9.5 Bq L⁻¹), then the mean pore water residence time would be 9.2 days, which is 1.4 to 2.1 \times longer than our mean residence times (Table 1). The maximum width and depth of our study beaches is roughly half that of the study beach of Swarzenski and Izbicki, so this longer mean residence time seems a reasonable estimate.

In a study of radon-determined beach pore water residence times on Santa Catalina Island, located off the coast of southern California, Colbert et al. measured pore water radon and equilibrium radon activities ranging from 0.5 to 2.1 Bq L⁻¹ and 2.8 to 3.7 Bq L⁻¹, respectively.¹⁷ The equilibrium radon sample collected closest to the waterline with highest silt content was 7.0 Bq L⁻¹. Both our pore water radon and equilibrium radon activities are higher than their measured ranges, but our highest equilibrium radon activity (6.9 Bq L⁻¹) is similar to their highest equilibrium activity (7.0 Bq L⁻¹) (Table 1). The coastal bluffs that back our study beaches are marine sedimentary rocks such as shales, siltstones, and mudstones, and their weathering products, silts and clays, comprise about 0.5% of Santa Barbara beach sediments.²⁰ These fine-grained sediments can enhance ²²⁶Ra adsorption due to higher surface area to volume ratios and cation exchange capacities relative to coarser-grained sediments such as sands.^{29,31} Thus, a higher proportion of fine-grained beach sediments may explain our higher overall radon activities and equilibrium radon activities. However, despite dissimilar radon and equilibrium radon activities, pore water residence times in the Santa Catalina Island beach were similar to ours, ranging from 0.7 to 2.0 days seaward and 3.3 to 8.0 days landward of the high tide line. About three-quarters (74%) of our residence times fall within this range (Table 1). This indicated that while beach sediment ²²⁶Ra content may have differed, perhaps due to sediment compositional differences, comparable physical forcing (i.e., tides) resulted in a similar extent of pore water circulation and residence times.

Pore Water DIN Speciation. Ammonium was the primary form of DIN in beach pore water (SI Table S1; Figure S1). Pore water had a lower dissolved oxygen concentration (73 ± 30 μ M vs 253 ± 17 μ M) and higher DOC concentration (241 ± 201 μ M vs 121 ± 47 μ M) than nearshore seawater, indicating potentially high oxidic respiration rates³² that could be sustained by high DOC concentrations (SI Table S1; Figure S1). Low pore water dissolved oxygen could also be a product of the oxidation of reduced iron along the top of the pore water table where oxidic infiltrating seawater meets suboxic pore water.³³ The rapid development (within 2–3 h of pore water sampling) of reddish-orange solids (iron oxyhydroxides) in $\sim 50\%$ of our pore water samples indicated the likelihood of this dissolved oxygen consumption pathway. Either or both of these dissolved oxygen consumption processes likely resulted in suboxic pore water conditions that favored ammonium persistence over nitrate.³⁴

Dissolved Inorganic Nitrogen (DIN) Temporal Evolution in Pore Water. We coupled radon residence times with pore water dissolved organic carbon (DOC) and dissolved

inorganic and total dissolved nitrogen (DIN and TDN) analyses to reveal the temporal evolution of the pore water DIN concentration, thereby expanding on the utility of radon as a residence time tracer in beach pore water environments.¹⁷ To accomplish this, we used modeled DOC:TDN ratios from the radon data set (Figure 2a) and the negative exponential

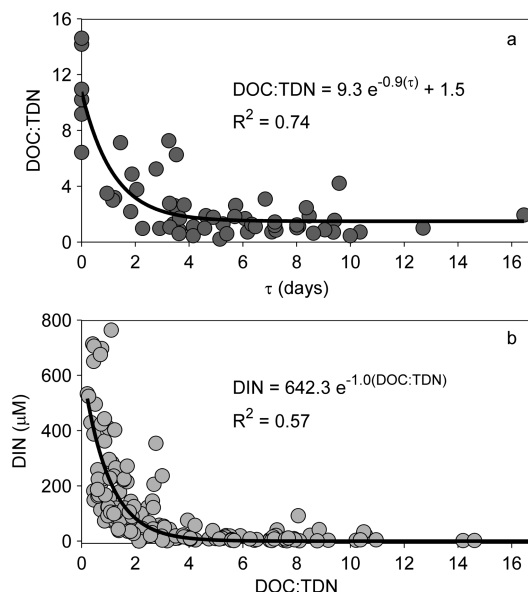


Figure 2. (a) Negative exponential relationship between pore water dissolved organic carbon (DOC) to total dissolved nitrogen (TDN) ratio and residence time ($n = 59$). (b) Negative exponential relationship between pore water dissolved inorganic nitrogen (DIN) concentration and DOC:TDN ratio ($n = 166$).

relationship between DIN and DOC:TDN (Figure 2b) for the entire data set to calculate DIN concentrations over the range of observed residence times in beach pore water (Figure 3a). Further, we used two combinations of the equilibrium DOC:TDN ratio (1.5 in Figure 2a) from the radon data set, and DIN y-intercept (642 μ M in Figure 2b) from the overall data set, to capture the range in observed DIN concentrations. To model the highest (lowest) DIN concentrations, we used the lower 95% CI (upper 95% CI) estimate of the equilibrium DOC:TDN ratio of 0.9 (2.1), and upper 95% CI (lower 95% CI) estimate of the DIN y-intercept of 767 μ M (518 μ M). These modeled DIN temporal evolution (i.e., DIN-te) curves are shown as “DIN-te (high)” (“DIN-te (low)”) curves in Figure 3a. The DIN-te curves showed that the pore water DIN concentration was initially ~ 10 μ M in infiltrating seawater (i.e., mean of seawater DIN concentrations), and rapidly increased between ~ 1 and 3 days, attaining asymptotically maximum DIN concentrations ranging from a low of 60 μ M (DIN-te low) to a high of 312 μ M (DIN-te high) around 3 days, remaining more or less constant thereafter (Figure 3a).

Volume-Weighted Mean (VWM) Dissolved Inorganic Nitrogen (DIN) Concentrations. With knowledge of the temporal evolution of the DIN concentration, radon residence times can be used to determine the volume-weighted mean (VWM) DIN concentration of pore water, which represents the DIN concentration of pore water discharge to the coastal ocean. Although the pore water volume in the beach is unknown, the proportion of the pore water volume with

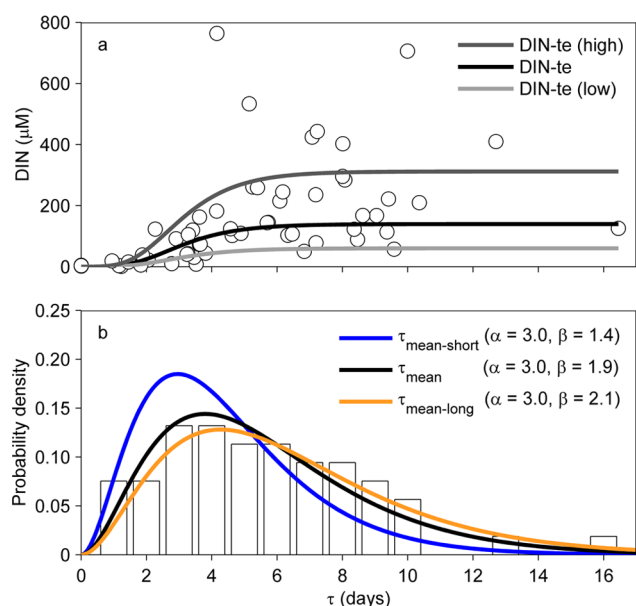


Figure 3. (a) Seawater and pore water dissolved inorganic nitrogen (DIN) concentration vs residence time. The three modeled DIN-te (i.e., DIN temporal evolution) curves were calculated using the modeled DOC:TDN ratio vs residence time (Figure 2a) and DIN vs DOC:TDN relationships (Figure 2b). (b) Modeled pore water residence time probability density distributions (gamma) for three observed mean pore water residence times; shortest (4.4 days), overall mean (5.7 days), and longest (6.4 days). Empirical pore water residence time distribution for entire radon data set (i.e., overall mean) shown as histogram (bars).

residence time equal to or less than a given residence time τ can be described by the cumulative RTD:³⁵

$$v(\tau) = V \int_0^{\tau} P(\tau) d\tau \quad (5)$$

where τ = pore water residence time (days), v = volume of pore water with residence time $\leq \tau$, V = total volume of pore water within a defined beach domain, and P = pore water residence time cumulative probability density function. The derivative of the pore water residence time cumulative probability density function P is the pore water probability density function p , which defines the probability density at any residence time τ . Therefore, if V is normalized to 1 (VV^{-1}), then the proportional pore water volume equal to τ within the defined beach domain is given by the residence time probability density at τ , and the pore water VWM DIN concentration can be calculated as

$$\text{VWM DIN} = \int_0^n p(\tau) \text{DIN}(\tau) d\tau \quad (6)$$

where VWM DIN = pore water volume-weighted mean DIN concentration (μM), p = pore water residence time probability density at τ , and DIN = pore water DIN concentration at τ .

A Kolmogorov–Smirnov test showed that the two-parameter gamma distribution was a good fit to the pore water RTD ($D = 0.06$; $p = 0.98$). We used the shape parameter α (3.0) from the modeled RTD for the overall radon data set ($n = 53$) to model two additional RTDs using the shortest and longest mean residence times observed for pore water sampling events ($\beta = \tau_{\text{mean}}\alpha^{-1}$), thereby representing the observed range in pore water RTDs (Table 1; Figure 3b). We used these three probability density distributions of pore water residence times (Figure 3b), in combination with the DIN-te modeled curves

(Figure 3a), to calculate pore water VWM DIN concentrations according to eq 6 (Table 2). VWM DIN concentrations

Table 2. Volume-Weighted Mean (VWM) Dissolved Inorganic Nitrogen (DIN) Concentrations (μM) for Combinations of Three DIN-te curves (Figure 3a) and Three Pore Water Residence Time Distributions (RTDs) (Figure 3b)

		DIN-te low	DIN-te	DIN-te high
mean τ short	(4.4 days)	37	87	194
mean τ	(5.7 days)	44	102	227
mean τ long	(6.4 days)	46	107	238

account for both residence time and DIN concentration variability in beach pore water since they are the integrated product of the RTDs and DIN-te curves.

An important consideration in the calculation of pore water VWM DIN concentrations is the potential inflation of residence time determinations, due to higher radon fresh groundwater mixing with lower radon recirculating seawater, which alters the DOC:TDN vs residence time relationship and RTD used to calculate the VWM DIN. For the 17 of 53 samples that contained fresh groundwater in our radon data set, we calculated that the mean difference between fresh groundwater corrected and uncorrected (i.e., no fresh groundwater influence) pore water residence times was 1.5 ± 2.4 days, with a median difference of 0.4 days. In turn, these residence time differences resulted in a maximum absolute difference and maximum percent difference in the VWM DIN concentration of 5 μM and 2.8%, respectively (see SI for description of analysis). We note that this minor effect on VWM DIN concentrations may not be the case along coastlines with a greater fresh groundwater influence or significantly higher fresh groundwater radon activity. However, for saline circulation cells in beaches along such coastlines, and for predominantly marine-influenced coastlines, VWM DIN concentration estimates should be similarly insensitive to uncertainty in the fresh groundwater radon activity.

An additional consideration in calculation of VWM DIN concentrations is that the RTD is not the same as the transit time distribution (TTD). The transit time describes the time elapsed from the initial infiltration of a volume of pore water into beach sands to its ultimate exfiltration to the coastal ocean, versus the residence time which describes the time elapsed from the initial infiltration of a volume of pore water into beach sands to the location of its extraction. Therefore, the TTD provides the most accurate estimate of the VWM DIN concentration of pore water discharge. However, the similar mean residence times for the fore and back beach, 5.4 and 6.2 days, respectively, and similar shape of the residence time distributions (i.e., gamma; $D_{\text{front}} = 0.10$, $p = 0.83$, $n = 34$ and $D_{\text{back}} = 0.11$, $p = 0.95$, $n = 19$) (Figure 4b and c) indicated that the overall RTD was a close approximation to the TTD (Figure 4a). If this were not the case, we would expect to observe a significant shift toward shorter residence times in the fore beach RTD, as the fore beach is both the hydrologic source and sink region where seawater infiltrates and exfiltrates our marine-dominated study beaches. Such a shift to lower residence times in the fore beach would also cause a larger difference in mean residence times and distributional shape between the fore and back beach RTDs, which we did not observe (Figure 4b and c).

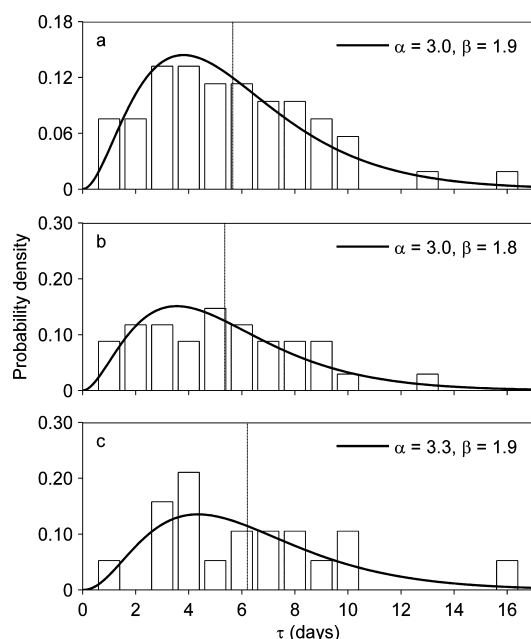


Figure 4. Pore water residence time probability density distributions for (a) entire radon data set ($n = 53$), (b) fore beach (normalized shore-perpendicular distances >0.5 ; $n = 34$), and (c) back beach (normalized shore-perpendicular distances <0.5 ; $n = 19$) regions with fitted gamma distributions. Mean pore water residence times shown as vertical dashed lines.

VWM DIN Concentration Variability in Beach Pore Water. Tides exert a dominant control on pore water circulation in all coastal regions with SGD, regardless of the proportion of recirculating seawater versus fresh groundwater.^{6,7,19,36,37} This tidal effect was evident in our study as a positive correlation between pore water mean residence time and tidal amplitude ($r^2 = 0.69$; $F_{1,4} = 10.7$; $p = 0.03$; Figure 5).

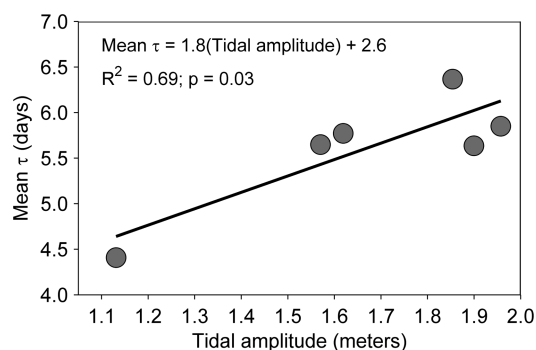


Figure 5. Mean pore water residence time (τ) vs tidal amplitude relationship with fitted linear equation for East Campus and Manzanita study beaches ($n = 53$). Tidal amplitude was calculated as the difference between higher high and lower low tidal elevations (semidiurnal tide) for the day on which individual pore water sampling events occurred.

The tidal amplitude was measured as the height difference between the higher high and lower low tide for the days on which pore water sampling was conducted. These variations in tidal amplitude resulted in a VWM DIN concentration (for a given DIN-te curve) for the RTD modeled using the longest mean residence time that was $1.2\times$ (20%) higher than that modeled using the shortest mean RTD (Table 2). However,

the 20% VWM DIN increase due to shifting RTDs does not account for variation in pore water discharge over the tidal cycle. Since tidal amplitude is positively correlated with mean pore water residence time (Figure 5) and pore water discharge,^{6,19,37} an increase in tidal amplitude over the neap-spring transition would not only result in a shift from the shortest mean RTD to the longest mean RTD, but also an increase in pore water discharge. This concurrent shift would therefore increase the pore water DIN flux (i.e., DIN flux = VWM DIN \times discharge) beyond our estimated 20% VWM DIN concentration increase.

A $5.2\times$ (420%) increase in the VWM DIN concentration resulted from a shift from the DIN-te low to high curve (for a given RTD) (Table 2). Macroalgal deposition onto Santa Barbara beaches, composed predominantly of *Macrocystis pyrifera* (giant kelp), is hypothesized to be a major source of POM, DOM, and DIN in beach pore water,^{22,38} and may in large part be the cause of the DIN-te shift (Figure 3a). Other POM and DOM loading events, such as nearshore phytoplankton blooms, could also cause enrichment of the pore water DIN concentration and DIN-te shifts.^{11,12} The larger VWM DIN increase caused by a DIN-te curve shift (420%) relative to a RTD shift (20%) is likely a function of the microtidal regime in Santa Barbara, which resulted in relatively low variation in pore water residence times and RTDs (Table 1; Figure 3b). Therefore, in coastal regions that have microtidal regimes, variation in POM and DOM loading may be a primary determinant of VWM DIN concentrations and variability in recirculating seawater. The largest increase in the VWM DIN concentration was observed with a concurrent shift from the shortest to longest mean RTD (Figure 3b) and from the DIN-te low to high curve (Figure 3a), resulting in a $6.4\times$ (540%) increase in the VWM DIN concentration. A giant kelp deposition event or nearshore phytoplankton bloom occurring over a neap to spring tidal transition (i.e., increasing tidal amplitudes) could result in such a VWM DIN concentration increase.

Our study demonstrates that variability in pore water RTDs and DIN vs residence time relationships (DIN-te curves) can interactively influence the pore water VWM DIN concentration, and that the resultant differences in VWM DIN concentrations can range from 1.2- to 6.4-fold, equivalent to 20–540% increases, respectively, from the minimum to maximum VWM DIN concentrations over the range in RTDs and DIN-te curves (Table 2). This suggests that using a single end-member DIN concentration to calculate SGD DIN flux over periods longer than the time scale of pore water residence times and flushing can result in errors by failing to account for interactive pore water hydrologic and biogeochemical dynamics. Since SGD contains a high volumetric proportion of recirculating seawater (ranging from 50% to $>99\%$) in coastal regions both with and without significant fresh groundwater contributions,^{6–9} accounting for temporal variability in the pore water RTD and DIN concentration is necessary to obtain accurate estimates of DIN delivery to coastal oceans. Perhaps more importantly though, using radon as a residence time tracer may reveal the temporal biogeochemical dynamics of other compounds to provide a better understanding of the dual role of beach pore water environments in mitigating land-derived pollutants and maintaining coastal marine biogeochemical cycles.

■ ASSOCIATED CONTENT

■ Supporting Information

Details of nearshore seawater and beach pore water dissolved oxygen sample collection and analysis, summary of pore water analytes for all study beaches (Table S1), residence time vs concentration relationships for DOC, ammonium, dissolved organic nitrogen (DON), and nitrate (Figure S1), and details of analysis of fresh groundwater influence on radon residence times and VWM DIN concentrations (Tables S2 and S3, Figures S2 and S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ NOTE ADDED AFTER ASAP PUBLICATION

This article published November 26, 2014 with an error in a figure of the Supporting Information file. The corrected file published December 8, 2014.