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JGR

Journal of Geophysical Research: Oceans

RESEARCH ARTICLE

10.1002/2015JC011221

Special Section:
Physical Processes Responsible for Material Transport in the Gulf of Mexico for Oil Spill Applications

Key Points:
- Increase in nutrient concentration might not always enhance oil biodegradation in beach
- High application rate improved subsurface oxygen condition for oil biodegradation in beach
- Optimal solution application duration existed for oil bioremediation in a given beach environment

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Citation:
Geng, X., Z. Pan, M. C. Boufadel, T. Ozgokmen, K. Lee, and L. Zhao (2016), Simulation of oil bioremediation in a tidally influenced beach: Spatiotemporal evolution of nutrient and dissolved oxygen, *J. Geophys. Res. Oceans*, *121*, doi:10.1002/2015JC011221.

Received 11 AUG 2015
Accepted 6 MAR 2016
Accepted article online 11 MAR 2016

Simulation of oil bioremediation in a tidally influenced beach: Spatiotemporal evolution of nutrient and dissolved oxygen

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Abstract Numerical experiments of oil bioremediation of tidally influenced beach were simulated using the model BIOMARUN. Nutrient and dissolved oxygen were assumed present in a solution applied on the exposed beach face, and the concentration of these amendments was tracked throughout the beach for up to 6 months. It was found that, in comparison to natural attenuation, bioremediation increased the removal efficiency by 76% and 65% for alkanes and aromatics, respectively. Increasing the nutrient concentration in the applied solution did not always enhance biodegradation as oxygen became limiting even when the beach was originally oxygen-rich. Therefore, replenishment of oxygen to oil-contaminated zone was also essential. Stimulation of oil biodegradation was more evident in the upper and midintertidal zone of the beach, and less in the lower intertidal zone. This was due to reduced nutrient and oxygen replenishment, as very little of the amendment solution reached that zone. It was found that under continual application, most of the oil biodegraded within 2 months, while it persisted for 6 months under natural conditions. While the difference in duration suggests minimal long-term effects, there are situations where the beach would need to be cleaned for major ecological functions, such as temporary nesting or feeding for migratory birds. Biochemical retention time map (BRTM) showed that the duration of solution application was dependent upon the stimulated oil biodegradation rate. By contrast, the application rate of the amendment solution was dependent upon the subsurface extent of the oil-contaminated zone. Delivery of nutrient and oxygen into coastal beach involved complex interaction among amendment solution, groundwater, and seawater. Therefore, approaches that ignore the hydrodynamics due to tide are unlikely to provide the optimal solutions for shoreline bioremediation.

1. Introduction

Oil release from the Macondo well MC252 following the Deepwater Horizon accident has been recognized to cause severe contamination of the GOM's beaches [*Atlas and Hazen*, 2011; *Boufadel et al*., 2011a; *King et al*., 2015]. Although major efforts are commonly placed on removing the maximum possible amount of oil using physical means, oil would still persist in the beaches at residual amounts. The ultimate fate of the residual oil depends on microorganism mediated oil degradation (i.e., biodegradation) [*Kostka et al*., 2011; *Joye et al*., 2014; *Kimes et al*., 2014]. Previous studies demonstrated that dissolved oxygen and nutrients are the key factors for hydrocarbon biodegradation to occur; limited availability of either of these factors would slow down the biodegradation rate [*Young*, 1984; *Wilson and Bouwer*, 1997; *Xia et al*., 2007; *Boufadel et al*., 2010]. The oxygen concentration needed for aerobic oil biodegradation is 2.0 mg/L [*Borden et al*., 1989; *Chiang et al*., 1989]. The nutrient (nitrogen) concentration for maximum aerobic oil biodegradation has been reported to be in the range of 2.5–10 mg/L [*Boufadel et al*., 1999a; *Du et al*., 1999; *Xia et al*., 2007; *Geng et al*., 2014].

Bioremediation is an active acceleration of the natural attenuation of oil pollutants. It has hence been commonly viewed as a natural or "green solution" to the problem of oil pollutants that causes, if any, minimal ecological effects [*Atlas*, 1995; *Atlas and Philp*, 2005]. While it cannot instantly or fully mitigate environmental impacts of an oil spill, due to its minimal physical disruption of oil-contaminated sites, minor adverse environmental impacts, less labor intensive, and lower costs in comparison to other technologies (e.g., high- and low- pressure spraying, steam cleaning, and manual scrubbing), bioremediation technology for beach

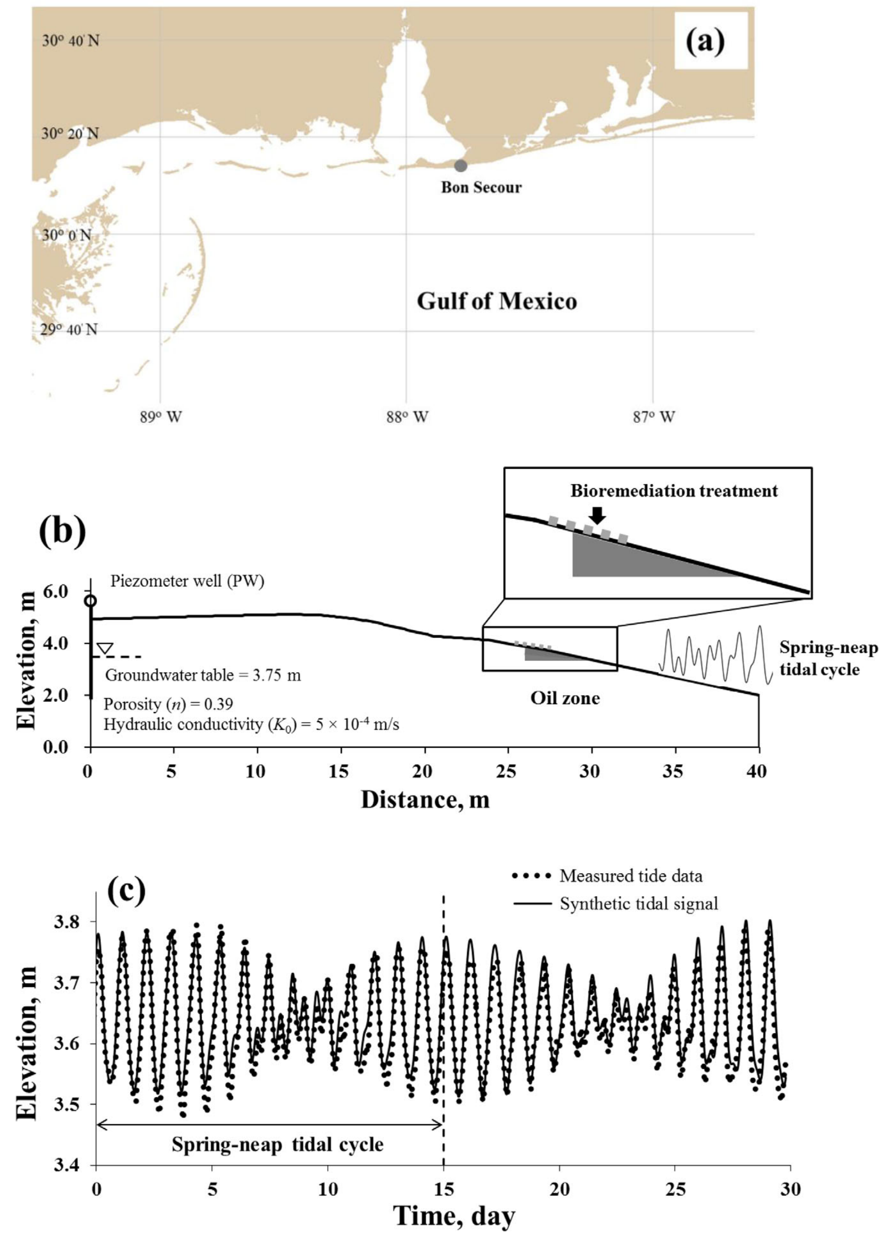

Figure 1. (a) Location of the studied beach in Bon Secour National Wildlife, Alabama. (b) Cross-sectional view of transect in the Bon Secour beach. The transect is perpendicular to the shoreline and a piezometer well was set up landward to measure the groundwater level. (c) Measured tide data from NOAA station 8730667 (http://tidesandcurrents.noaa.gov/stationhome.html?id=8730667) along with the synthetic tidal signal used to simulate the tide fluctuations. Note that the tidal period selected for the fitting of the synthetic tidal signal is 30 days in September 2014.

cleanup has become increasingly attractive. Various strategies for bioremediation of oil-contaminated beaches have been implemented in previous studies. Recent studies suggest that the presence of dispersant could adversely affect oil biodegradation [*Kleindienst et al*., 2015]. But it is assumed herein that the oil in the beach has no dispersant on it, and thus, its biodegradation is not affected by dispersant. The introduction of exogenous microbes (i.e., bioaugmentation) might be beneficial in areas where indigenous microorganisms grow slowly or are unable to degrade a particular hydrocarbon. However, only *Tsutsumi et al*. [2000] confirmed the effectiveness of this approach for enhancing the shoreline oil biodegradation. By contrast, a field study by *Venosa et al*. [1996] and a review by *Zhu et al*. [2001] indicated that bioaugmentation did not accelerate the rate of biodegradation over biostimulation.

Table 1. Characteristics of the Numerical Experiments

Case	Application Duration, d	Application Rate of Amendment Solution, L/h
1		
2	30	30
3	7	30
4	14	30
5	60	30
6	90	30
7	30	15
8	30	60

Biostimulation has been proven to accelerate oil biodegradation and widely adopted for shoreline bioremediation [*Sendstad*, 1980; *Eimhjellen et al.*, 1982; *Eimhjellen and Josefsen*, 1984; *Lee and Levy*, 1989; 1991; *Venosa et al.*, 1996], although it might cause eutrophication due to excess nutrient addition [*Smith et al.*, 1999]. *Venosa et al.* [1996] conducted a bioremediation test in Delaware in which light crude oil was intentionally released onto the beach; they found that a nitrogen concentration of 3–6 mg/L in the interstitial pore water enhanced hydrocarbon biodegradation from two to three folds than the natural attenuation rate where pore water nitrogen concentrations averaged 0.8 mg/L.

While bioremediation has been successfully implemented in numerous oil-contaminated coastal sites [*Swannell et al.*, 1996; *Venosa et al.*, 1996; *MacNaughton et al.*, 1999; *Chaerun et al.*, 2004; *Gallego et al.*, 2006], the fate of applied nutrient solution along with its mixing with near-shore groundwater in tidally influenced beaches has not yet been fully elucidated. Tidally influenced beaches are highly dynamic, and tide actions induce a complex mixing between water emanating from inland sources and the sea [*Moore*, 1999; *Slomp and Van Cappellen*, 2004; *Boufadel et al.*, 2006; *Robinson et al.*, 2006; *Li et al.*, 2008]. The application of solutions onto beaches involves complex processes of flow and solute transport as tidal action would alter residence time and pathways of applied solute in the beach. Therefore, it is essential to have a rigorous conceptual physically based model to capture the salient features of each process. The result of such an approach would be very important for spill responders to design effective bioremediation strategies and to quantitatively evaluate specific response alternatives.

Using the numerical code BIOMARUN, *Geng et al.* [2015] conducted various simulations on a typical oil-contaminated beach in the Gulf of Mexico, and found that different limiting factors affected different portions of the beach. In the upper intertidal zone, where the inland incoming nutrient concentration was large, oil biodegradation occurred deeper in the beach. In the midintertidal zone, a reversal was noted where the biodegradation was fast at shallow locations, and it was due to the decrease of oxygen with depth due to consumption, which made oxygen the limiting factor for biodegradation. However, a bioremediation strategy was not taken into account in their study. In order to explore a potential bioremediation strategy for this beach, this paper used the model BIOMARUN model [*Geng et al.*, 2015] to simulate a bioremediation strategy that adding nutrient and dissolved oxygen to stimulate biodegradation of low solubility hydrocarbon trapped in the beach intertidal zone, and then performed multiple numerical experiments to further examine the key factors (e.g., nutrient treatment's duration and application rate) likely affecting the efficiency of oil bioremediation on coastal beaches. The simulation results were analyzed to provide insight into the design of bioremediation strategies and associated complex behavior of subsurface oil biodegradation and solute fate in beach aquifers.

2. Methodology

2.1. The BIOMARUN Model

The model BIOMARUN couples the model MARUN, which is a 2-D finite element model (vertical slice) for density-dependent flow and solute transport in variably saturated media [*Boufadel et al.*, 1999b], with the model BIOB, a multiplicative Monod model for low solubility hydrocarbon biodegradation [*Geng et al.*, 2013, 2014]. The model can solve up to eight equations including subsurface water flow, the transport and fate of dissolved salt, nutrient (e.g., nitrogen or phosphorus), oxygen (or any electron acceptor such as sulfate), and two types of substrates and associated degraders (i.e., one equation for each type of substrate or degraders). In the BIOMARUN model, the equations of water flow and fate and transport are discretized in space by the Galerkin finite element method [*Pinder and Gray*, 1977] using linear triangular elements and integrated in time using backward Euler with mass lumping [*Celia et al.*, 1990]. The governing equations of the BIOMARUN model were fully described in *Geng et al.* [2015].

Table 2. Increase in Oil Removal Efficiency, %[a]

Case	Alkanes	Aromatics
1		
2	65	47
3	23	14
4	42	29
5	69	65
6	69	65
7	48	37
8	76	61

[a]Increase in oil removal efficiency is calculated based on equation (3).

2.2. Numerical Simulation of Oil Biodegradation in a Sandy Beach

The simulation was based on a field study conducted in a sand beach located in Bon Secour National Wildlife Refuge, Alabama (Figures 1a and 1b). The beach is primarily composed of uniformly fine- to very fine-grained sand. It is impacted by tidal action ranging from 0.15 m (at neap tide) to 0.3 m (at spring tide, Figure 1c). The field measurements reported in our previous work [*Geng et al.*, 2015] were used herein as input for the modeling study in this paper. A Thermos Scientific, RDO optical probe and an ORION 4 Plus hand-held meter (Thermo Scientific, Beverly, MA) were used for DO measurements. The oxygen concentration measured in the pore water and the sea was 8.2 mg/L, close to the solubility limit of oxygen in water in contact with air [*Gilbert et al.*, 1968]. Nutrient (i.e., NO_2^-/NO_3^-) concentrations were measured in the lab using an AutoAnalyzer3 (Seal Analytical, Mequon, WI). The average concentration of nitrogen was 1.2 ± 0.34 mg-N/L in the beach and 0.2 mg-N/L in the sea. This is much lower than the optimal concentration (2.0–10.0 mg-N/L) to support near-maximum growth of hydrocarbon-degrading microorganisms [*Venosa et al.*, 1996; *Boufadel et al.*, 1999a; *Wrenn et al.*, 2006]. Detailed information on the measurements is described in *Geng et al.* [2015].

The tide data were obtained from NOAA station 8730667, which is 19.2 km northeast of the studied site (http://tidesandcurrents.noaa.gov/stationhome.html?id=8730667). As we needed continuous tide data to be used as input to MARUN, we assumed that the tide is represented by five harmonic components, consistent with prior works [*Guo et al.*, 2010; *Li and Boufadel*, 2010; *Xia et al.*, 2010]. Thus, the truncated Fourier series below was fitted to the tide data:

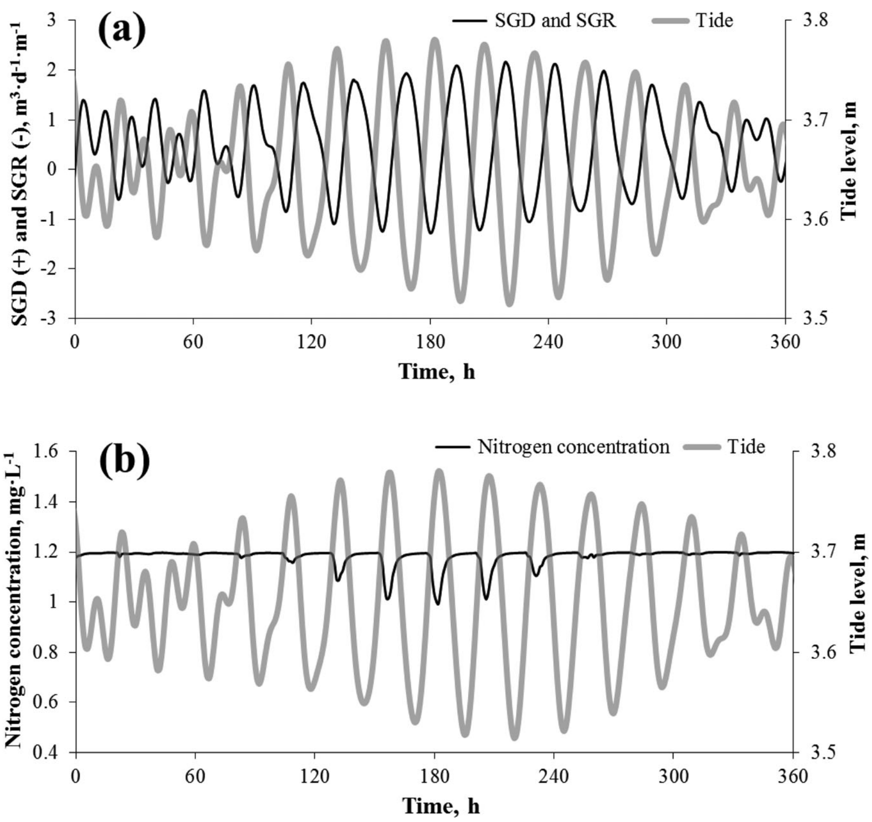

Figure 2. Simulated temporal variation of (a) submarine groundwater recharge (SGR) and discharge (SGD) across the beach face and (b) the preoiling concentration of nitrogen within the oil-contaminated zone.

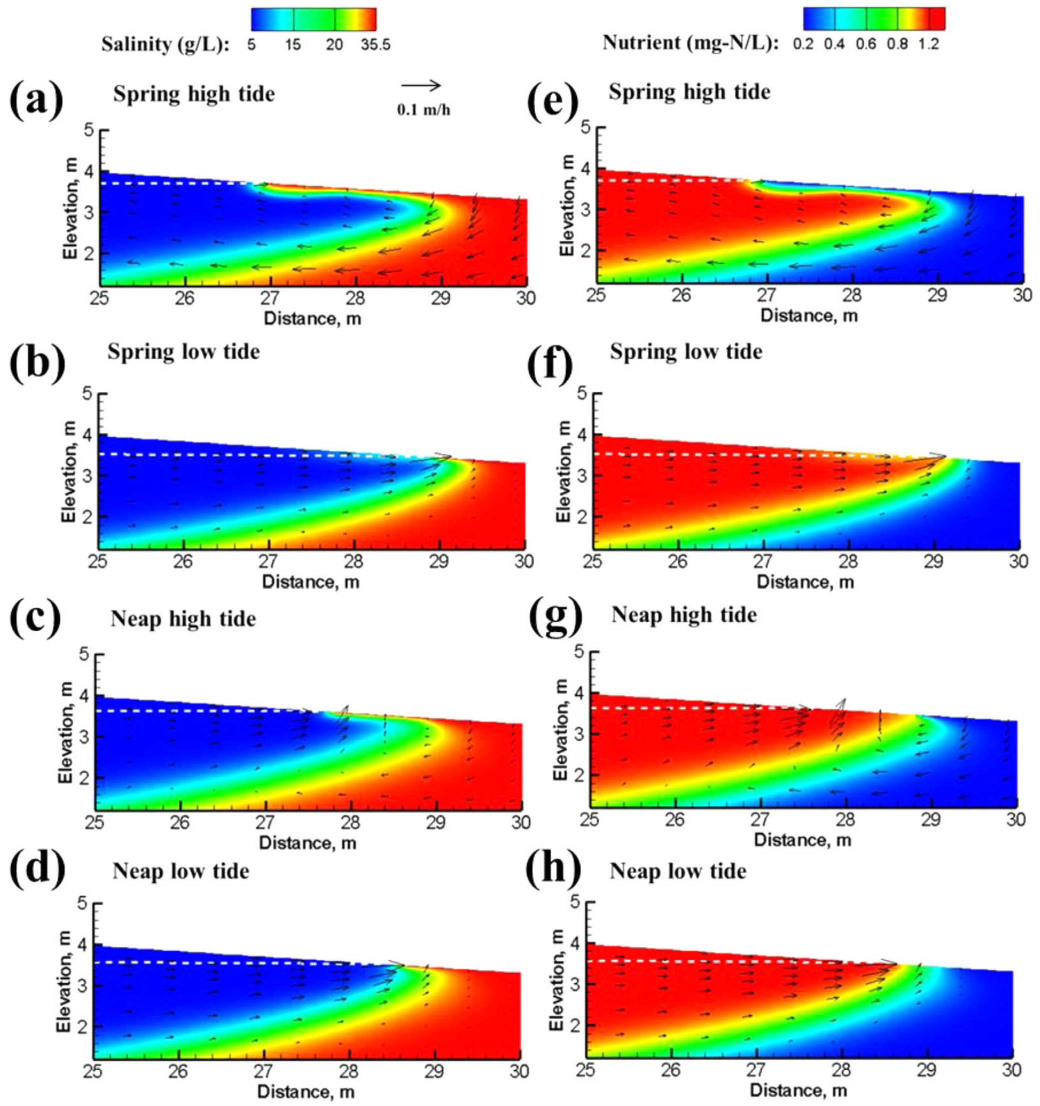

Figure 3. Simulated concentration contours of (a-d) salinity and (e-h) nitrogen at four different times in spring-neap tidal cycle. The concentration of salt and nitrogen is 5.0 g/L and 1.2 mg-N/L in inland groundwater, and 35.5 g/L and 0.2 mg-N/L in seawater, respectively.

$$H_{Sea}(t)=H_0+\sum_{i=1}^{5}A_i\cos(\omega_i t-\varphi_i), \tag{1}$$

where H_{Sea} [L] is the tidal level and H_0 [L] is the mean sea level; the parameters A_i, ω_i and φ_i are the amplitude [L], tidal frequency [T^{-1}], and phase [rad] of ith tidal constituent, respectively. The tidal duration selected for the fitting of the synthetic tidal signal is 30 days from 1 to 30 September 2014, which captured a complete spring-neap tidal cycle. The predicted tide data based on equation (1) are reported in Figure 1c, and they show good visual agreement with the tide gauge data.

2.3. Numerical Implementation

The simulated domain is 40 m long and with depth varying from 2 to 6 m depending on the topography of the beach (shown in Figure 1b). Formation of small sand ripple on the beach due to oceanic forcing was not considered in our simulation, which might impact beach topography and alter subsurface flow and solute fate [*Harms*, 1969]. It is observed that the oil that emanated from the Macondo 252 well was deposited on the beach during storms, and buried by sands during subsequent storms [*Operational Science Advisory Team (OSAT)*, 2011; *Boufadel et al.*, 2011a]. As our focus is the intertidal zone, the spatial distribution of the

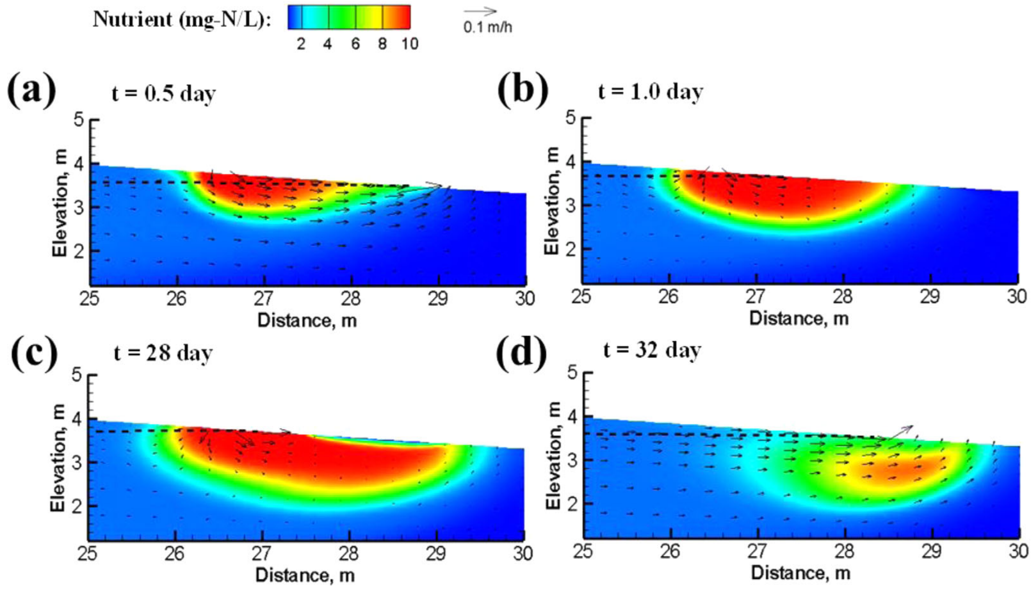

Figure 4. Simulated nitrogen concentration contours at four different times after initiation of bioremediation treatment (Case 2). The applied nitrate concentration was 10 mg-N/L.

oil was assumed uniform following a wedge shape of maximum thickness 0.5 m at highest high tide line, which is the same as the assumption proposed in *Geng et al*. [2015]. We assumed the concentrations of alkanes and PAHs were 100 mg/kg of sediment and 50 mg/kg of sediment, respectively, which indicates low-level oil contamination within the beach [*Kostka et al*., 2011]. Measured average nutrient and oxygen concentrations were used as inland and seaside boundary conditions for transport simulation. As the vadose zone is well aerated, and the concentration of oxygen in air is ~38 times that of the solubility limit of dissolved oxygen (in water) per unit volume, we assumed that the dissolved oxygen is in equilibrium with the atmosphere (i.e., equal to 8.2 mg/L) at all beach locations where the air content ratio is greater than 0.3 (i.e., the moisture ratio is less than 0.7). In the model, as the beach is variably saturated due to tide, moisture saturation was checked throughout the beach at each time step and dissolved oxygen concentration of 8.2 mg/L was assigned to the zone where moisture ratio is less than 0.7. Hydrocarbon degraders typically attach to sediments [*Holm et al*., 1992; *Johnson et al*., 1995], and for this reason, they were assigned a large retardation coefficient. Also, a constraint was imposed on the model to make certain that the microbial degrader does not decay to less than the (initial) background concentration X_B (i.e., 2×10^{-2} mg/kg sediment and 2×10^{-4} mg/kg sediment for alkane and PAH degraders, respectively), whose values were measured in nonoiled zone of the beach. This is commonly done in modeling hydrocarbon biodegradation within sediments [*Essaid et al*., 1995; *Schirmer et al*., 2000; *Geng et al*., 2014].

The parameter values used for the simulation of beach hydraulics and hydrodynamics have been reported in *Geng et al*. [2015] (Table 1). Bioremediation was assumed to occur as a result of "application" of solution laden with 10 mg-N/L of nutrient (i.e., nitrogen) and 8.2 mg/L of dissolved oxygen onto the upper intertidal zone of the beach (between $x = 26.3$ m and $x = 26.8$ m). The boundary conditions for describing this process can be expressed as:

$$q|_{(x,z)\in\Gamma_{app}} = 30\ L/h, \qquad \text{if} \quad t \in P_{app}, \tag{2a}$$

$$c_{oxy}|_{(x,z)\in\Gamma_{app}} = 8.2\ mg/L, \quad \text{if} \quad t \in P_{app}, \tag{2b}$$

$$c_{nut}|_{(x,z)\in\Gamma_{app}} = 10\ mg/L, \quad \text{if} \quad t \in P_{app}, \tag{2c}$$

where q is application rate, Γ_{app} is application segment of the beach, c_{oxy} is applied dissolved oxygen concentration, c_{nut} is applied nutrient concentration, and P_{app} is the period of the treatment. Simulations were also conducted to examine the key factors (nutrient treatment's duration and application rate) likely affecting the bioremediation of oil in tidally influenced beaches. The duration and application rate used for each

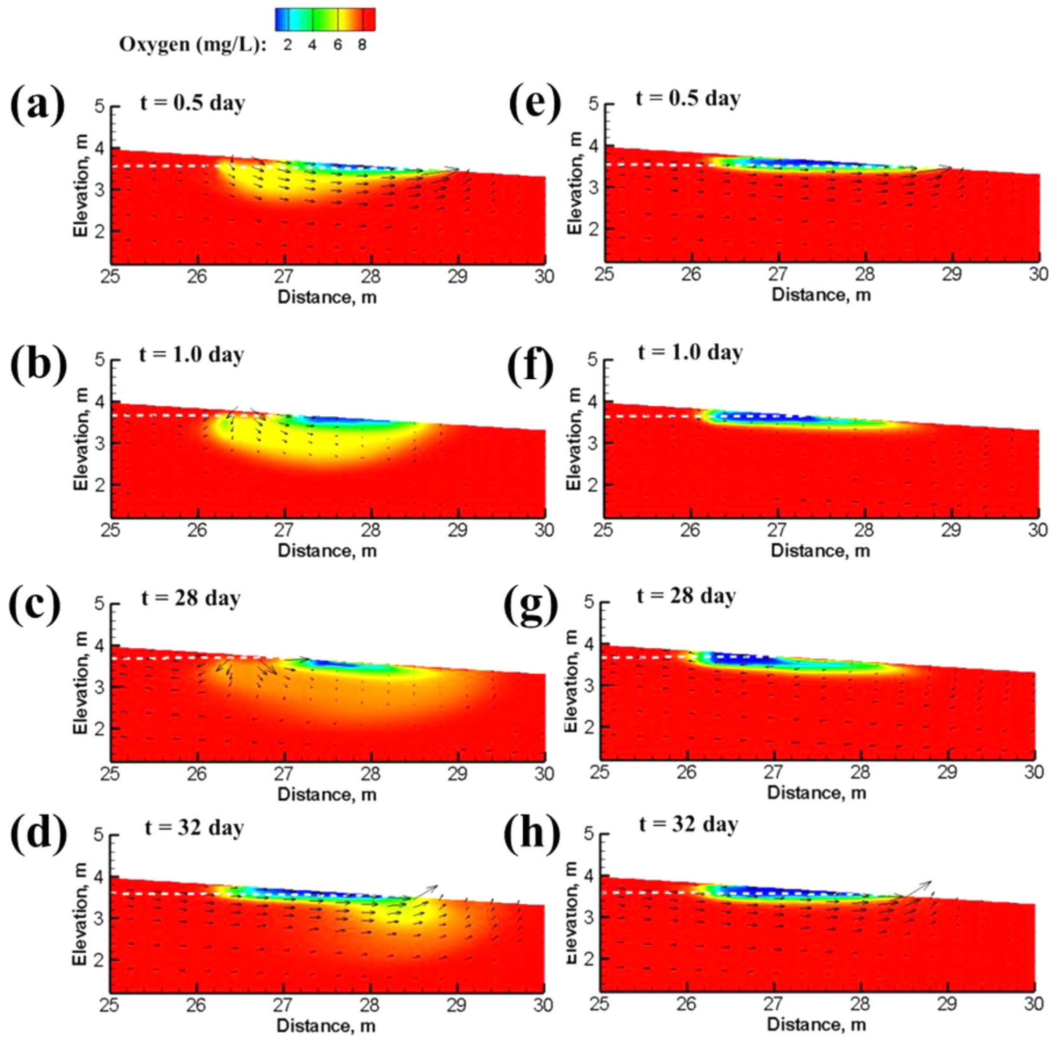

Figure 5. Simulated concentration contours of oxygen varied due to (a–d) natural attenuation (i.e., Case 1) and (e–h) bioremediation (i.e., Case 2) at four different times. The dissolved oxygen is 8.2 mg/L, which is the same as that in seawater.

bioremediation case are summarized in Table 1. The improvement of oil removal efficiency due to the bioremediation was characterized by the following expression:

$$I_{ORE}=100\%\times(T_1-T_i)/T_1,\quad i=2\text{–}8, \tag{3}$$

where I_{ORE} denotes the increase in oil removal efficiency due to bioremediation; T_1 and T_i denote the time for 85% of oil mass to be removed from the beach by natural attenuation (i.e., Case 1) and the bioremediation strategy adopted (i.e., Case i), respectively. The results are summarized in Table 2. For all the simulations, the model BIOMARUN was first run approximately for 100 days without oil until the hydraulic and hydrodynamic regime reached a quasi-steady state. The pressure and solute distribution were then used as initial conditions for the simulation of nutrient and dissolved oxygen application for oil bioremediation, which was run over a simulation time of 200 days.

2.4. Biochemical Retention Time Map

The concept of the biochemical retention time map (BRTM) was introduced by *Geng and Boufadel* [2015] to quantify the effective role of nutrients in a beach system. The underlying idea is that beyond a certain threshold value for nutrient or oxygen, there would be no positive effect on oil biodegradation. Thus, if the pore water concentration of 2.5 mg-N/L provides maximum oil biodegradation, then having the concentration above 2.5 mg-N/L has no practical effect on oil biodegradation, yet it would increase the residence

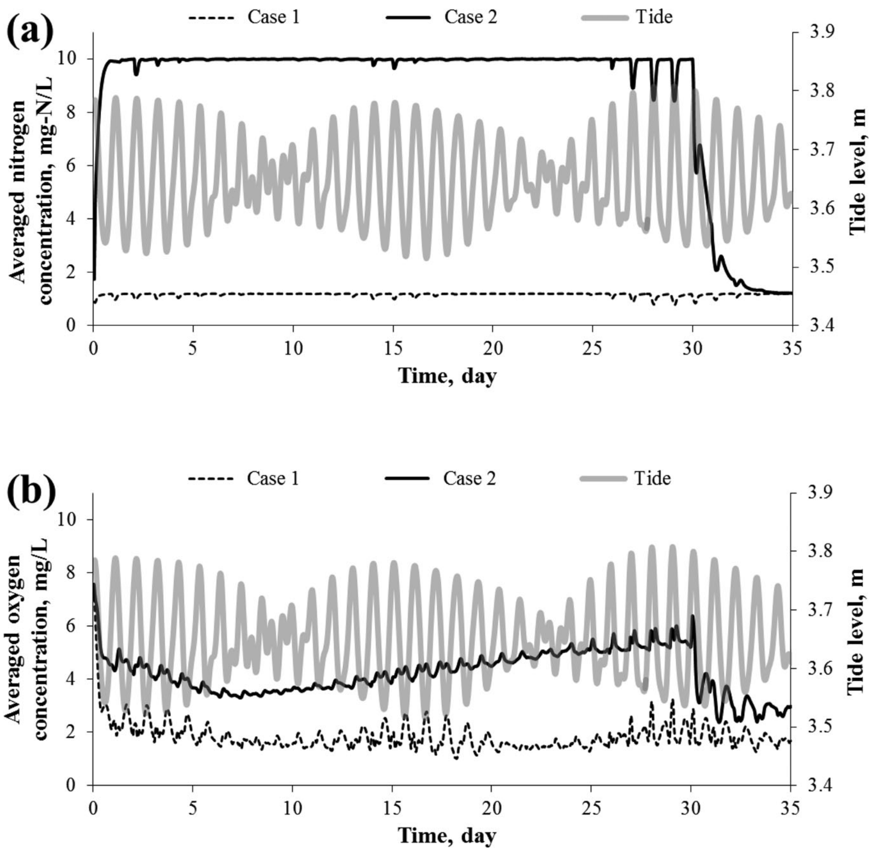

Figure 6. Simulated temporal variation of the average concentration in the initially oiled zone of (a) nutrient and (b) oxygen for Case 1 (i.e., natural attenuation) and Case 2 (i.e., bioremediation).

time of the plume in the beach suggesting that it actually enhanced oil biodegradation. For this reason, to characterize the effective residence time of solute within the beach for oil biodegradation, one should use the minimum concentration of nutrient (or oxygen) that is large enough to engender maximum oil biodegradation [*Boufadel et al*., 1999a; *Geng et al*., 2014].

The biochemical retention time map (BRTM) is delineated based on the simulation results (i.e., biochemical retention time) at each computation node as follows:

$$BRT(x,z)=\frac{\int_{\tau=0}^{\infty}\tau\min\left(C_t(x,z,\tau),C_{Th}\right)d\tau}{\int_{\tau=0}^{\infty}\min\left(C_t(x,z,\tau),C_{\mathrm{Th}}\right)d\tau} \tag{4}$$

where the integration time of infinity is used for generality, but a time of 200 days is used herein. The term C_t (*x*, *z*, *t*) represents a threshold concentration of relevance to delineate the edge of the plume, while C_{Th} (threshold) is the concentration above which, no practical enhancement in biological activity takes place.

3. Results and Discussion

3.1. Circulating Flows and Solute Transport

Simulations were conducted in the absence of oil to reveal the dynamics of exchange and mixing between terrestrial groundwater and seawater, circulating flow rate across the beach face and subsurface solute distribution and transport. Figure 2a shows temporal variation of submarine groundwater discharge (SGD) and recharge (SGR) across the beach face. The simulated seawater-groundwater exchange varied from $\sim$2.1 m^3·d^{-1}·m^{-1} at the spring tide to $\sim$1.0 m^3·d^{-1}·m^{-1} at the neap tide, which is relatively small in comparison to the values obtained from previous studies on sandy beach aquifers [*Burnett et al*., 2003; *Michael*

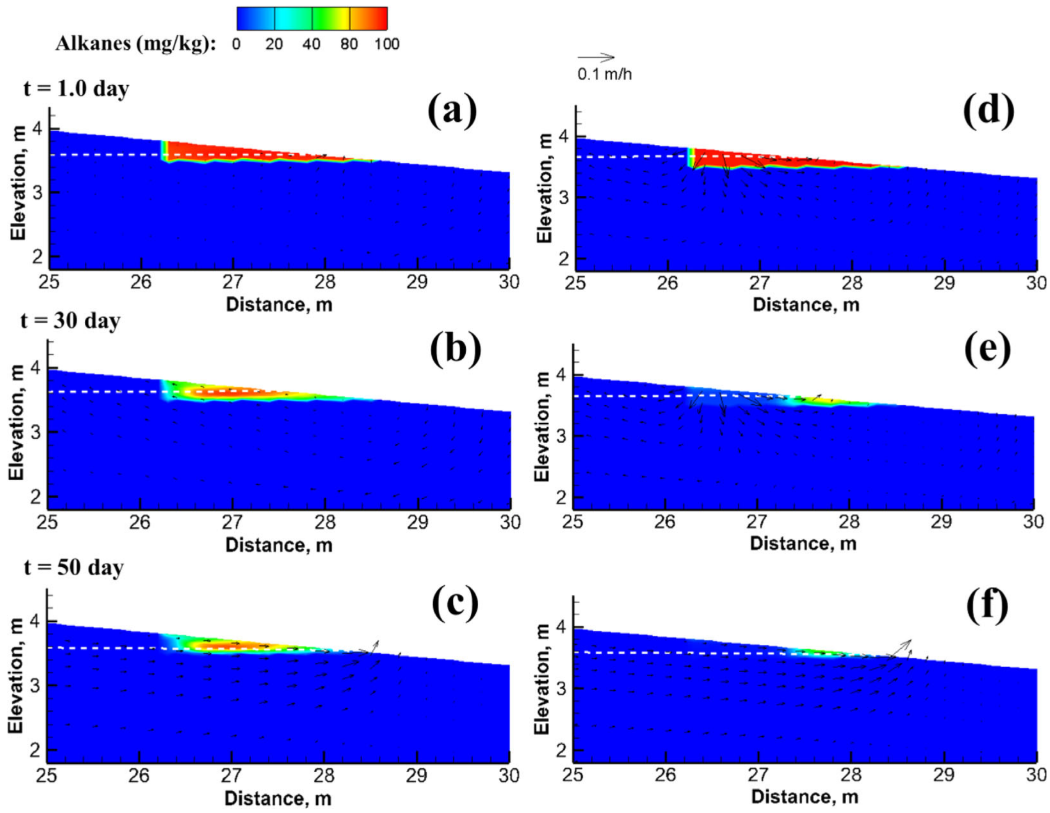

Figure 7. Simulated concentration contours of alkanes at different times (t = 1, 30, and 50 days) for (a–c) Case 1 (i.e., natural attenuation) and (d–f) Case 2 (i.e., bioremediation).

et al., 2005; *Robinson et al*., 2007a]. This is probably due to the small tidal range of 0.3 m in our studied beach. The seawater-groundwater exchange would alter geochemical condition in the beach intertidal zone due to distinct geochemical properties in seawater and terrestrial groundwater. Figure 2b shows the preoiling concentration of nitrogen within the oil-contaminated zone. The results indicate that the nitrogen concentration was almost the same as that in terrestrial groundwater (i.e., 1.2 mg/L) at neap tides. In contrast, during the spring tidal cycles, the average nitrogen concentration decreased from 1.2 mg/L to 1.0 mg/L at high tides. It is because spring high tides drove much low-nitrogen seawater (i.e., 0.2 mg/L) into the beach and thereby decreased subsurface nitrogen concentration. The results indicate temporal response of intertidal geochemistry conditions to tidal action. As shown in Figure 3, an upper saline/low-nutrient plume was formed at the spring high tide and then washed out at the subsequent low tide. In contrast, during the neap tide cycle, the upper plume had less landward expansion at the high tide due to the small tidal range. The results also show that the upper plume had different subsurface extent for salt and nutrient, especially at the neap high tide. It is due to different mixing concentration between seawater and freshwater. Compared to nutrient, seawater (35.5 g/L) and terrestrial groundwater (5.0 g/L) induced a larger density gradient driving salt to transport in the beach and thereby resulted in a more apparent upper saline plume at high tides. Our simulation results demonstrated that the beach intertidal zone involved very complex seawater-groundwater recirculation and mixing [*Robinson et al*., 2007b; *Abdollahi-Nasab et al*., 2010; *Boufadel et al*., 2011b; *Santos et al*., 2012; *Heiss and Michael*, 2014]. It caused different level of influence on subsurface solute (e.g., salt and nitrogen) concentration structure at different tidal stage. Therefore, investigating the interaction between seawater and freshwater should be the first step for one to understand pore water chemistry and its associated role in biogeochemistry reactions in coastal beaches.

3.2. Implementation of Bioremediation Treatment

Subsurface fate and transport of applied nutrient and dissolved oxygen are key factors for designing an effective bioremediation strategy for oil-contaminated beach aquifers. Figure 4 shows the simulated

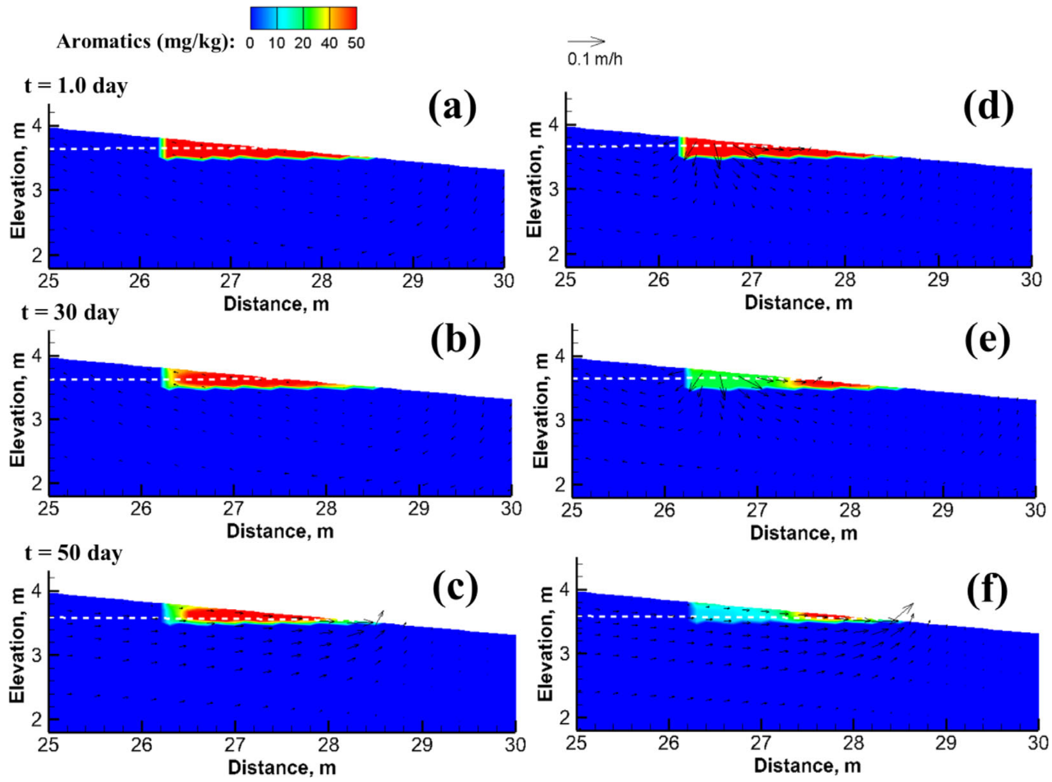

Figure 8. Simulated concentration contours of aromatics at different times (t = 1, 30, and 50 days) for (a–c) Case 1 (i.e., natural attenuation) and (d–f) Case 2 (i.e., bioremediation).

subsurface nutrient transport and distribution after the bioremediation treatment at four different time points. The nutrients were first "applied" at t = 0. The results show that high nutrient plume expanded in subsurface as the bioremediation treatment was implemented onto the beach (Figures 4a–4c). The high nutrient plume was defined as that possessing a concentration above 2.0 mg-N/L, which provides maximum oil biodegradation. The subsurface expansion was faster in the first few days due to advective transport of the solute, and then slowed down as the plume migrated downward when dispersion dominated the transport of the solute. After the application ceased at t = 30 d, the high nutrient plume contracted due to the dilution by surrounding groundwater, and discharged from the beach low tide mark into the ocean at the subsequent falling tides (Figure 4d). The results suggest that although the residence time of solute in the beach was mainly controlled by duration of the solution application, tidal action seemed to play an important role in the residence time of applied solute after the bioremediation implementation. Rather than discharging directly along the beach surface, the solute was pushed downward by tidal action and thereby had to follow a long pathway to discharge from the beach into the ocean. Besides residence time, the subsurface expansion of applied solution was also affected by tidal actions. At t = 28 days, the high nutrient plume was overlaid by low nutrient water due to the seawater infiltration during the rising tide (Figure 4c). The mixing between applied solution (10 mg-N/L) and infiltrated seawater (0.2 mg-N/L) at subsequent falling tide could alter the plume concentration. Therefore, our results point out that tidal action needs to be considered during the bioremediation treatment. The importance of tidal action on subsurface solute/contaminates fate and transport in coastal beach aquifers has also been recognized in previous studies [*Robinson et al*., 2009; *Huettel et al*., 2014].

Simulated subsurface oxygen transport and distribution at four different time points with and without bioremediation treatment is shown in Figure 5. It is observed that unlike nitrogen, low oxygen plume appeared in the oiled zone even the bioremediation was implemented onto the beach (Figures 5a–5d). The reason is that the oxygen consumption was much more than nitrogen during the aerobic biodegradation [*Geng et al*., 2013, 2015]. However, compared to natural attenuation, the oxygen condition in the oil zone was significantly improved. In particular, at the upper intertidal zone, dissolved oxygen concentration reached

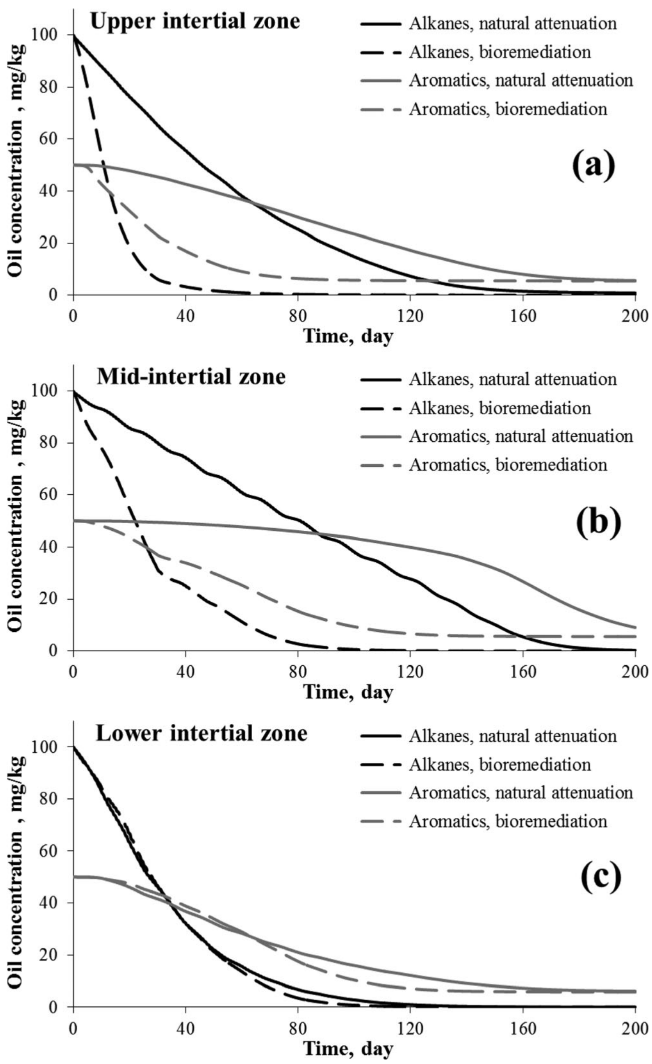

Figure 9. Simulated temporal variation of oil concentration at different portion of the intertidal zone by bioremediation and natural attenuation. The upper, mid-, and lower intertidal zone is between 26.3 m and 27 m, between 27 m and 27.7 m, and between 27.7 m and 28.5 m, respectively.

8.0 mg/L due to the bioremediation application, while the concentration was below 2.0 mg/L under natural attenuation. This is because the bioremediation applied plenty of dissolved oxygen into the beach, which compensated to some extent oxygen depletion due to the oil biodegradation. Also, the application of the amendment solution onto the beach prompted advective and dispersive transport of solutes and facilitated the mixing of the low oxygen plume with surrounding groundwater, which improved oxygen condition of the oiled zone. The improvement of oxygen condition due to the bioremediation was more evident in proximity of the upper intertidal zone. It is because the application of high nutrient and oxygen solution was directly implemented to the upper intertidal zone (between $x = 26.3$ m and $x = 27$ m), where without bioremediation treatment, the oxygen replenishment only occurred during spring high tide due to seawater infiltration. In contrast, in the lower intertidal zone (between $x = 27.7$ m and $x = 28.5$ m), oxygen replenishment occurred deep in the beach. It is because the solution application was not directly implemented to that zone.

To further illustrate the effects of bioremediation on nutrient and dissolved oxygen condition in the oil-contaminated zone, the temporal concentration variation of nutrient and oxygen within the oiled zone for the cases with and without bioremediation are reported in Figures 6a and 6b. The nutrient concentration in the oiled zone was significantly improved by the bioremediation treatment. After the treatment, the concentration increased from 1.1 mg-N/L to 10 mg-N/L within a day, and leveled off until the end of the treatment. Notice that the concentration slightly dropped during the spring high tide. This is because spring high tides drove low-nutrient seawater (0.2 mg-N/L) into the beach, and subsequently diluted the high nutrient plume formed by continuous bioremediation application for 30 days. Without bioremediation treatment, the oxygen concentration averaged in the oiled zone remained at $\sim$1.8 mg/L, and fluctuated slightly with tides. This is in contrast to the oxygen concentration of $\sim$4.0 mg/L when bioremediation was implemented onto the beach. The results indicate that the bioremediation treatment, in general, doubled the oxygen concentration averaged in the oiled zone. Notice that large oxygen depletion was shown between $t = 5$ days and $t = 10$ days for the case with the bioremediation treatment. It is because a significant amount of oil was degraded within that period (shown in later section, Figure 9).

The enhancement of nutrient and dissolved oxygen condition implies the improvement of oil removal efficiency from the beach owing to the bioremediation. This is consistent to the oil removal efficiency reported in Table 2 that the bioremediation stimulated biodegradation of alkanes and aromatics to be 65% and 47%

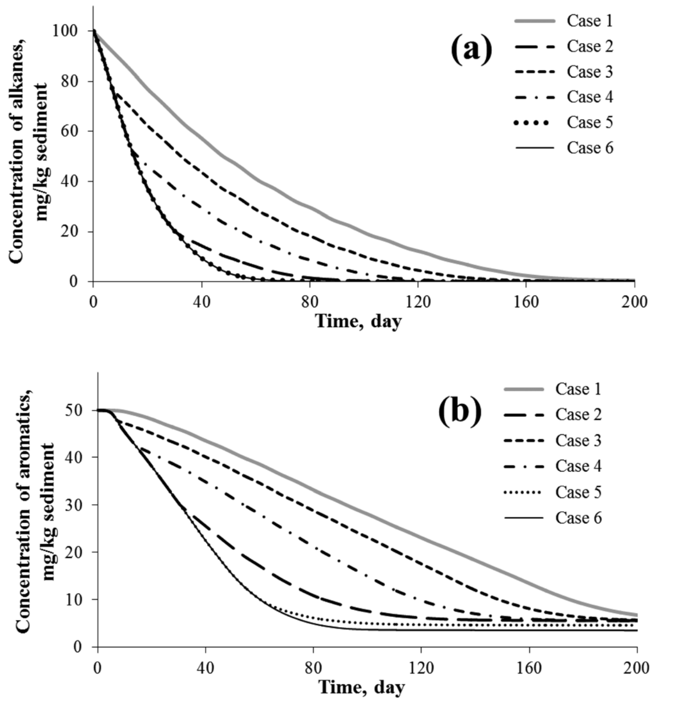

Figure 10. Simulated temporal variation of (a) alkane and (b) aromatic concentration for the cases with different treatment duration. The case of natural attenuation (i.e., Case 1) is shown for comparison.

faster than natural attenuation, respectively. It is observed that the impacts of bioremediation treatment on oil biodegradation were distinct at different beach portions (Figure 7). In particular, the oil trapped in the upper and midintertidal zone was completely biodegraded within 30 days in comparison to the persistence of considerable amount of oil under natural attenuation. The oil removal in the lower intertidal zone was not significantly improved by the bioremediation. It is because a considerable fraction of the applied solution left the beach prior to the low tide line, and the concentration that reached the lower intertidal zone was relatively low due to the dilution and the large consumption for oil biodegradation at the upper and midintertidal zone. Both of these factors affect adversely the nutrient and oxygen replenishments of the lower intertidal zone. The biodegradation of aromatics was slower in comparison to alkanes. However, it can still be observed that the aromatics biodegradation increased due to the bioremediation. After 30 days of the treatment, the aromatic concentration decreased to ~20 mg/kg of sediment at the upper and midintertidal zone, while that under natural attenuation was more than 80 mg/kg of sediment; only a small amount of aromatics biodegraded in the lower portion of the upper intertidal zone (Figure 8). Compared to alkanes, after 30 days of the bioremediation treatment, more aromatics were still present in the beach (discussed below). Therefore, in terms of the bioremediation treatment of aromatics, the duration needs to be longer due to slow biodegradation rate. The simulation results also indicate that tidal action altered flow pattern of the applied solution in the beach and thereby affected the delivery of nutrient and dissolved oxygen to the oil-contaminated zone. In particular, at the lower intertidal zone, the delivery of applied nutrient and dissolved oxygen to the oiled zone was from bottom to up, which is the reversed direction of the solution application. This impact would be even more significant in beach aquifers subjected to large tidal range.

The temporal variation of oil concentration at different portions of the beach is reported in Figure 9 to further reveal the spatial variation of oil removal efficiency due to the bioremediation. The oil concentration at the upper and midintertidal zones of the beach decreased dramatically during the bioremediation treatment (i.e., the first 30 days), which shows the significant improvement of oil removal efficiency at these zones through nutrient application. The oil removal efficiency was improved by 78% and 58% at the upper and midintertidal zones, respectively, due to the bioremediation. However, at the lower intertidal zone, compared to natural attenuation, the concentration of alkanes and aromatics for the case of bioremediation was even slightly higher in the first 50 days after which the concentration tended to decrease faster. Faster oil biodegradation at the upper and midintertidal zone caused significant oxygen consumption within the first 50 days when most oil trapped there was biodegraded. The subsequent induced low oxygen water at the upper and midintertidal zone migrated seaward and downward at subsequent falling tides and discharged from the beach near the low tidal mark. It degraded the oxygen condition at the lower intertidal zone and thereby induced slightly slower oil biodegradation there. After the most oil was biodegraded at the upper and midintertidal zone, high-oxygen water started to migrate to the lower intertidal zone and accelerate oil biodegradation there. At the mid intertidal zone, the curve showing alkane natural attenuation wiggled with time. It is due to the alternation of spring and neap tides. At spring tides, larger hydraulic exchange brought more oxygen-rich seawater into the beach, and thereby resulted in faster oil biodegradation (shown as concave segments); in contrast, the beach had less oxygen replenishment at neap tides due to smaller tidal range, which slowed down oil biodegradation (shown as convex segments). As expected, the effect was evident in the midintertidal zone of the beach due to the most frequent inundation and exposure during high tides and low tides. Compared to alkanes, the wiggles were not observed from the aromatic biodegradation. It is most likely due to its extremely low biodegradation rate, which mitigated the wiggles and made them undetectable in aromatic concentration variation.

3.3. Effects of Bioremediation Duration

The temporal concentration variation of alkanes and aromatics under various duration of continual application of nutrient solution shows that biodegradation was faster during the application period, and slowed down immediately after the treatment ceased (Figures 10a and 10b). When the duration reached 2 months, the removal of alkanes and aromatics was rising 69% and 65% faster than natural attenuation (Table 2), respectively, and further extension of the treatment duration did not affect the oil removal efficiency, which is due to the fact that most oil had been biodegraded within 2 months. Therefore, the results indicate that there is an optimal treatment duration for a given beach environment. Decreasing the duration would extend the persistence of oil within the beach, while increasing the duration would not further enhance oil removal efficiency. For this beach, natural attenuation reduced the oil concentration to almost zero within 6 months, while the bioremediation removed almost all the oil from the beach within 2 months.

The temporal variation of the high-nutrient plume area under different condition of treatment duration was simulated to reveal the subsurface expansion of applied solute in the beach (Figure 11a). The high nutrient plume was defined as that possessing a concentration above 2.0 mg-N/L. It is observed that the high nutrient plume only persisted in the beach during the bioremediation treatment. Once the application ceased, the nutrient concentration returned to prebioremediation condition within a few days. It was mostly due to the fact that rising tides diluted the high nutrient plume with seawater (0.2 mg-N/L) and falling tides caused the discharge of the plume into the ocean [*Li et al.*, 1999; *Boufadel*, 2000; *Geng and Boufadel*, 2015]. It is shown that the plume had large extent at spring tides and gradually shrunk as tidal range attenuated. The simulated results suggest that tidal action facilitated spreading of the nutrient plume and thereby expanded the bioremediation zone in the beach. The impacts of tidal actions on the plume spreading could be also observed in each tidal cycle. To illustrate this phenomenon, the results in several tidal cycles, delineated in Figure 11a using a black line box, was zoomed in and shown in Figure 11b. The spreading area increased during the rising tide and decreased during the

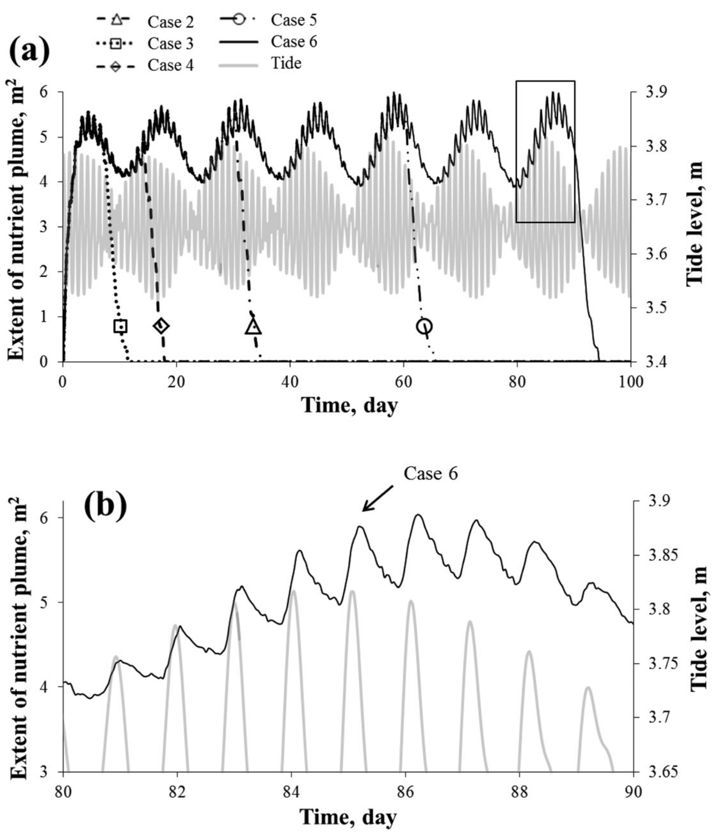

Figure 11. (a) Simulated temporal variation of spreading area of the high nutrient plume for the cases with different treatment duration. Note that the edge of the plume is delineated by 2.0 mg-N/L. The inset of Figure 11a is shown in Figure 11b.

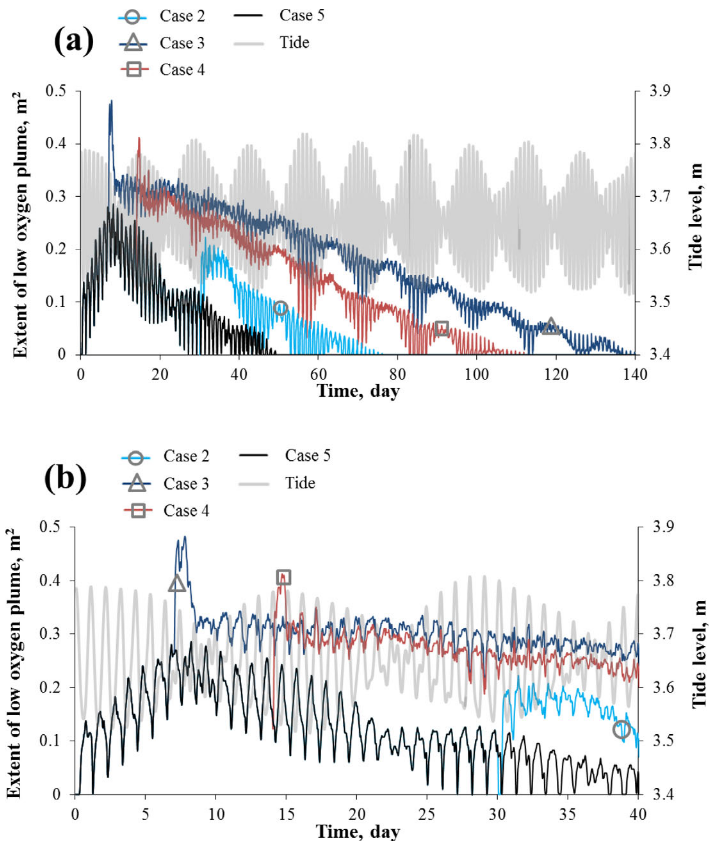

Figure 12. (a) Simulated temporal variation of spreading area of the low oxygen plume for the cases with different treatment duration. Note that the edge of the low oxygen plume is delineated by less than 2.0 mg/L. (b) The temporal variation of the extent of the plume in the first 40 days. Notice that the total area of the initially oiled zone is 0.66 m_2.

falling tide; meanwhile, the maximum spreading appeared after the high tide. The time delay is most likely due to the fact that after the high tide, the plume kept propagating landward due to the higher sea level than the groundwater table. The results also show that the plume spread more during the spring tidal cycle, which is to be expected, because large tidal ranges pushed the plume more landward and thereby caused more spreading in the beach [*Heiss and Michael*, 2014].

Compared to the nutrient plume, the temporal variation of spreading area of the low oxygen (concentration less than 2.0 mg/L) plume is completely different in the beach. As expected, the low oxygen plume persisted for a longer time with shorter treatment time. For each duration condition, the extent of the low oxygen plume increased as the bioremediation was started on the beach. After the bioremediation treatment ceased, the expansion of the low oxygen sharply increased in the first few days and then gradually decreased. The expansion of the low oxygen plume during the bioremediation is because that high nutrient application stimulated oil biodegradation and thereby caused large consumption of dissolved oxygen in the beach. After the bioremediation application creased, high nutrient condition still persisted for a few days as tidal action caused gradual discharge of the amendment solution from the beach. Therefore, oil biodegradation would still cause large consumption of dissolved oxygen in the beach, while the oxygen replenishment was less. It resulted in a sharp expansion of the low oxygen plume in the beach after the bioremediation ceased. However, as the high nutrient plume was gradually discharged from the beach, subsequent low nutrient condition in the oil-contaminated zone lowered oil biodegradation rate. It caused less consumption of dissolved oxygen in subsurface. Therefore, the extent of the low oxygen plume tended to be small. The sharp expansion of the low oxygen plume was not observed for the case with 2 months' bioremediation. This is because most oil had been biodegraded within 2 months.

The expansion of the low oxygen plume was also affected by tidal actions, as shown in Figure 12b, which reports the temporal variation of plume area in the first 40 days. It is observed that the low oxygen plume expanded at low tides and contracted at high tides. This is because rising tides drove seawater-laden oxygen into the beach, while during the low tide, no oxygen-rich water entered the oiled zone directly, albeit from the groundwater discharge. The results also demonstrate that the low oxygen plume area was smallest during the spring tidal cycle, because large tidal range drove more seawater into the beach. The results indicate that design of the bioremediation needs to be deliberated in coastal beach aquifers. It is because tides affect not only residence time and pathway of subsurface solute transport, but also subsurface solute spreading, which are crucial for an effective bioremediation implementation.

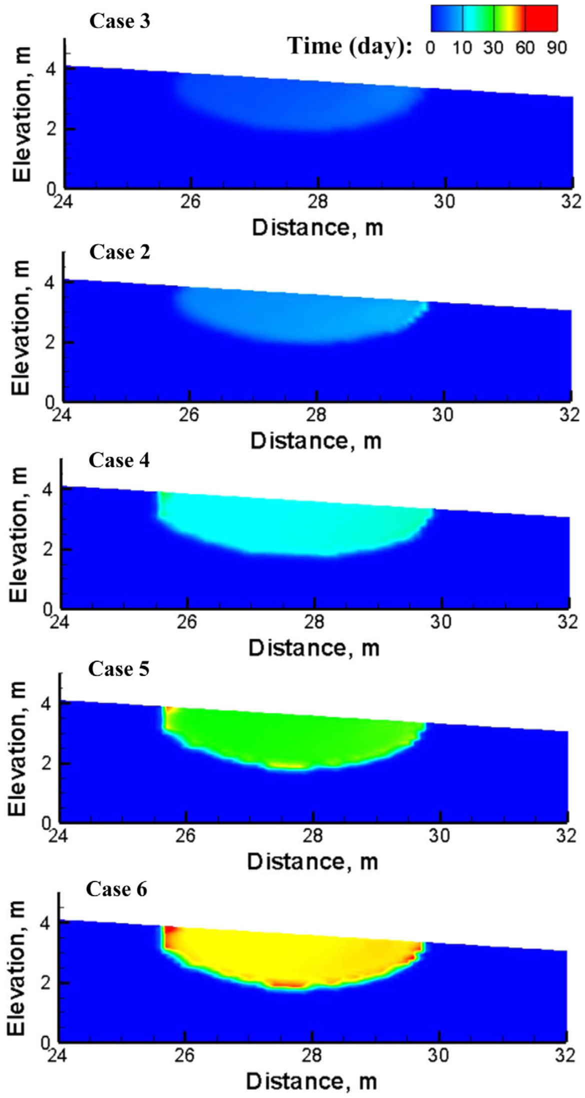

Figure 13. Simulated biochemical residence time map (BRTM) in the beach at CTh = 2.0 mg-N/L (equation (4)) for the cases using different treatment durations.

Simulated biochemical residence time map (BRTM) in the beach at $C_{th} = 2.0$ mg-N/L under different condition of the treatment time is shown in Figure 13 to characterize the effective residence time of solute within the beach for oil biodegradation. The residence time of high concentration nutrient in the beach was increased by extending the treatment time. Notice that the residence time of the solute was relatively longer at the edge of the map, which is probably due to the fact that the applied solute traveling along the edge had a longer trajectory prior to discharge from the beach. The expansion of the nutrient plume was almost the same for all bioremediation cases, indicating extending treatment time plays a minor role in altering the extent of remedial zone.

3.4. Effects of Bioremediation Application Rate

Temporal concentration variation of alkanes and aromatics at different application rate of the amendment solution shows that the oil biodegradation was significantly accelerated by increasing the application rate (Figures 14a and 14b). The removal efficiency was improved by 76% and 61% when 60 L/h of application rate was adopted onto the beach. This is because higher application rate provided more nutrient and oxygen to the oiled zone in unit time.

Temporal extent of the high-nutrient plume was simulated to reveal its response to different application rate of the nutrient solution (Figure 15a). It shows that higher application rate caused larger plume spreading in the beach. This is because higher application rate facilitated advective and dispersive transport of solute and thereby prompted the mixing of the nutrient-rich plume with the surrounding groundwater. The time for applied solute to discharge from the beach tended to be longer when higher application rate was adopted for the bioremediation. In particular, it took almost 1 month (i.e., two spring-neap tidal cycles) for applied nutrient to totally discharge from the beach when 60 L/h of the rate was applied for the bioremediation. The simulation results indicate that adopting higher application rate would cause longer postimpacts of excess nutrients on beach subsurface.

Different application rate of the amendment solution also altered the temporal behavior of the low oxygen plume in the beach (Figure 15b). Higher application rate improved the oxygen condition and reduced the expansion of the low oxygen plume in the beach. In particular, for the case with higher application rate, the spreading area of the low oxygen plume went down to 0.27 m^2 and 0.18 m^2 for the cases of 30 L/h and 60 L/h in comparison to 0.9 m^2 for the case of 15 L/h. This is because high nutrient application stimulated oil biodegradation and subsequently caused large oxygen consumption in the beach; while, lower application rate replenished less amount of dissolved oxygen into the beach and thereby caused large oxygen depletion in the beach. The results suggest that besides nutrient, replenishment of dissolved oxygen into the beach is also important for an efficient shoreline bioremediation treatment. Ambient condition of dissolve oxygen might be sufficient for natural attenuation in the beach. However, enhanced oil

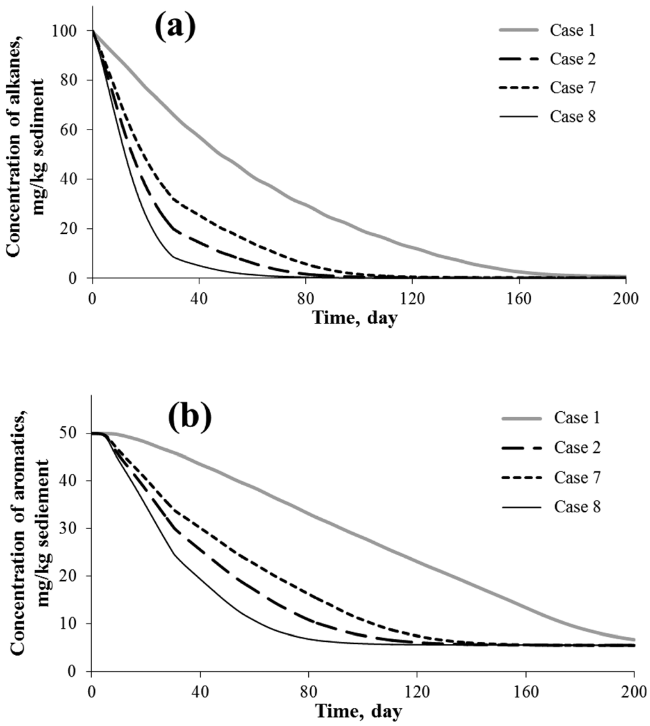

Figure 14. Simulated temporal concentration variation of (a) alkanes and (b) aromatics for the cases using different application rates for the bioremediation treatment. The case of natural attenuation (i.e., Case 1) is shown for comparison.

biodegradation rate due to nutrient addition would increase the demand of dissolved oxygen and might result in oxygen-limited environment for oil biodegradation in the beach.

Simulated biochemical residence time map (BRTM) in the beach at $C_{th} = 2.0$ mg-N/L at different application rate of the bioremediation treatment is shown in Figure 16. High nutrient plume had larger expansion for the case with higher application rate. Residence time of high nutrient was also affected by different application rate. In particular, for the case with the rate of 60 L/h, the residence time significantly increased at the lower intertidal zone of the beach compared to other cases. This is because that larger application rate prompted high nutrient plume to expand deeper in the beach. The solute driven to the deeper location would migrate longer time in the beach prior to discharge to the ocean.

Previous studies have showed that the key factors affecting the efficiency of shoreline oil bioremediation includes the concentration of applied nutrient solution and the contact time between the hydrocarbon and a sufficiently high concentration of nutrients [*Venosa et al*., 1996; *Wrenn et al*., 1997; *Venosa et al*., 2010]. There is a maximum nutrient concentration allowing oil biodegradation to proceed at the maximum rate. Additional increase in the concentration has no practical effect on microbial degradation. The concentration below this threshold limits microbial growth and thereby slows down oil biodegradation. Therefore, it is critical to maintain the optimal concentration in oiled regions for an effective bioremediation implementation. The contact time between the hydrocarbon and applied solute is also essential, because oil biodegradation is usually a relatively long term process. To design a feasible bioremediation strategy, one needs to ensure sufficient residence time of applied high nutrient solution in the oiled regions for optimal microbial degradation to persist. In general, BRTM presented from our work could provide a clear subsurface residence time distribution of solute at any given threshold concentration in beach aquifers, taking into account tidally driven recirculation and associated mixing dynamics among applied solution, groundwater, and seawater. Therefore, providing BRTM would instructive for spill responder to make a comprehensive design for shoreline oil-spill bioremediation.

4. Conclusion

The bioremediation of tidally influenced beaches contaminated with oil spill was investigated numerically in this work using an archetypical beach in the Gulf of Mexico with realistic tide conditions. Bioremediation was assumed to occur as a result of "application" of a nutrient solution onto the beach surface in the upper intertidal zone. As expected, the application significantly increased the nutrient concentrations in the beach and improved subsurface oil removal efficiency by 76% and 61% for alkanes and aromatics, respectively, in comparison to natural attenuation. However, enhanced oil biodegradation rate due to nutrient addition increased the demand of dissolved oxygen. It resulted in oxygen-limited environment for oil biodegradation even though the dissolved oxygen in the beach was sufficient for oil natural attenuation. Therefore, the replenishment of dissolved oxygen to the oil-contaminated zone is also essential for an effective bioremediation strategy. This means that increasing the nutrient concentration in the application solution without

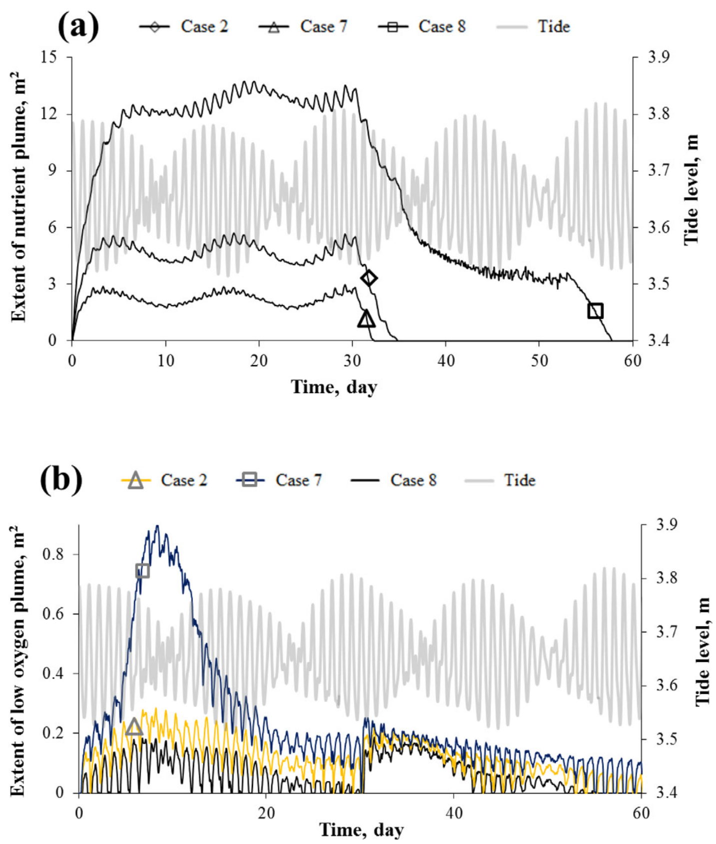

Figure 15. Simulated temporal variation of the spreading area of (a) the nutrient and (b) low oxygen plumes for the cases using different application rates for the bioremediation treatment. The edge of the nutrient plume was delineated by 2.0 mg-N/L, and the edge of the low oxygen plume was also delineated by 2.0 mg/L.

accounting for oxygen limitations would overestimate the extent of biodegradation, and result in nutrient waste. The simulation results revealed that the bioremediation treatment was more effective in the upper and midintertidal zone of the beach due to the proximity of the application location. In the lower intertidal zone, due to less nutrient and oxygen replenishment, bioremediation treatment had less impact there.

The effect of application duration was also investigated, and it was found that under continual application, most of the oil biodegraded within 2 months, while it persisted for 6 months under natural conditions. While the difference in duration suggests minimal long-term effects, there are situations where the beach would need to be cleaned for major ecological functions, such as temporary nesting or feeding for migratory birds [*Botton*, 1984; *Botton et al*., 1994; *Tsipoura and Burger*, 1999], and duration of a few months could make a major difference. In addition, our study assumed low-level oil contamination onto the beach. As bioremediation enhanced oil biodegradation rate which reduced the oil mass by ratio, the acceleration of oil biodegradation due to the bioremediation would be more evident for heavily oil-contaminated beaches.

A biochemical retention time map (BRTM), introduced by *Geng and Boufadel* [2015], is a spatial distribution of limiting biodegradation factors, such as nutrient. It accounts for the fact that low concentration of nutrient and oxygen decrease the biodegradation rate of oil, but also too high concentration do not affect the rate (as it becomes diffusion limited). On the latter point, relying only on the retention time (or residence time) of high concentrations at a particular location would overestimate biodegradation, as the microbes would be limited in uptaking the high concentration.

For the current work, the BRTM approach showed that extending the bioremediation time increased the effective residence time of high nutrient solution in the beach. However, it played a minor role in expanding subsurface high nutrient plume for oil bioremediation. The results also indicated that bioremediation prompted oil to biodegrade within a specific treatment duration in a given beach environment. In other

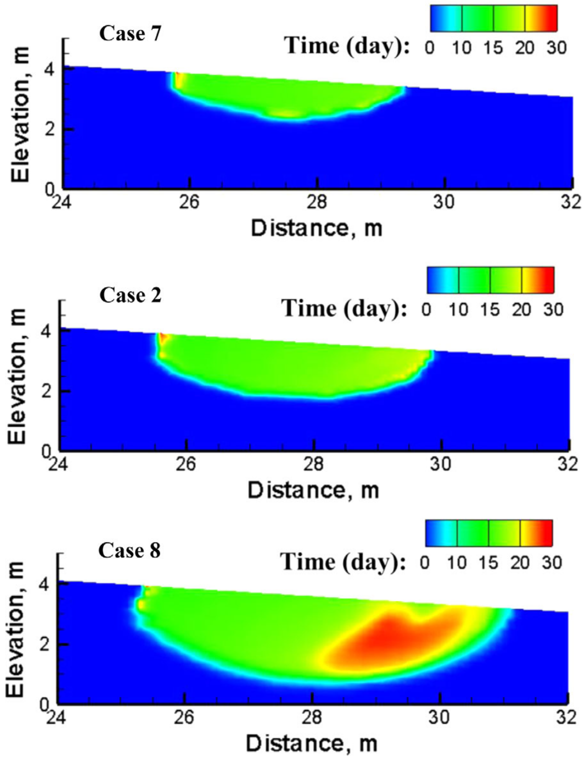

Figure 16. Simulated biochemical residence time map (BRTM) in the beach at CTh = 2.0 mg-N/L for the cases using different application rate for the bioremediation treatment.

words, the optimal duration for bioremediation was dependent upon the stimulated oil biodegradation rate. Shortening the duration would extend the oil persistence within the beach, while extending the duration would not further enhance oil removal efficiency, which is due to the fact that most oil had been biodegraded. Enhancing bioremediation application rate increased the expansion of the high nutrient plume in the beach. However, due to tidal action, adopting higher application rate would cause longer postimpacts of excess nutrients on beach subsurface. Therefore, the optimal application rate for bioremediation should depend upon the extent of oil-contaminated zone in the beach. The interaction of oil and mineral fines and organic matters, and the subsequent formation of oil particle aggregates (OPA) would dilute the concentration of oil per sediment mass, but it could also reduce the accessibility of oil to microorganisms and fresh supply of nutrients and oxygen. Therefore, the biodegradation of oil within OPA is not well understood, and is not considered herein. Dissolved organic matter (DOM) within sand beach is usually small at locations far from the Mississippi delta in the Gulf of Mexico. However, as the initial oil concentration is relatively small, the DOM could have played a role, and it is thus a shortcoming of the current study. Temperature could also be a factor affecting oil biodegradation in the beach. We aim to address this issue in future studies. Eutrophication due to nutrient addition is unlikely to occur in an open water environment, such as in the Gulf of Mexico whose shorelines are subject to waves, rip currents, longshore currents, and tidal exchanges.

Acknowledgments
This research paper was made possible, in part, by a grant from The Gulf of Mexico Research Initiative to the Consortium CARTHE II, and subsequently to the New Jersey Institute of Technology. Funding has also come from the National Science Foundation under grant CBET-1313185. However, no official endorsement should be implied from any of the funding entities. The data for this paper are available upon e-mail request (nrdpcenter@gmail.com) at Center for Natural Resources Development and Protection.

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