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Modeling Biodegradation of Subsurface Oil in Sand Beaches Polluted with Oil

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ABSTRACT 299532:

In April 2010, the explosion of the Deepwater Horizon (DWH) drilling platform led to the release of nearly 4.9 million barrels of crude oil into the Gulf of Mexico. The oil was brought to the supratidal zone of beaches (landward of the high tide line) by waves during storms, and was buried during subsequent storms. The objective of this paper is to investigate the biodegradation of subsurface oil in a tidally influenced sand beach located at Bon Secour National Wildlife Refuge and polluted by the DWH oil spill. Two transects were installed perpendicular to the shoreline within the supratidal zone of the beach. One transect had four galvanized steel piezometer wells to measure the water level. The other transect had four stainless steel multiport sampling wells that were used to collect pore water samples below the beach surface. The samples were analyzed for dissolved oxygen (DO), nitrogen, and redox conditions. Sediment samples were also collected at different depths to measure residual oil concentrations and microbial biomass. As the biodegradation of hydrocarbons was of interest, a biological model based on Monod kinetics was developed and coupled to the transport model MARUN, which is a two dimensional (vertical slice) finite element model for water flow and solute transport in tidally influenced beaches. The resulting coupled model, BIOMARUN, was used to simulate the biodegradation of total n-alkanes and polycyclic aromatic hydrocarbons (PAHs) trapped as residual oil in the unsaturated zone. Model parameter estimates were constrained by published Monod kinetics parameters. The field measurements, such as the concentrations of the oil, microbial biomass, nitrogen, and DO, were used as inputs for the simulations. The biodegradation of alkanes and PAHs was predicted in the simulation, and sensitivity analyses were conducted to assess the effect of the model parameters on the modeling results. Simulation results indicated that n-alkanes and PAHs would be biodegraded by 80% after 2 ± 0.5 years and 3.5 ± 0.5 years, respectively.

INTRODUCTION:

In April 2010, the explosion of the Deepwater Horizon (DWH) drilling platform led to the release of nearly 4.9 million barrels of crude oil into the Gulf of Mexico (Camilli et al. 2010). A significant portion of the released oil was transported to the Gulf shorelines (Kostka et al. 2011). The OSAT-2 report, released by the Operational Science Advisory Team, described the spatial oil distribution of the remained oil on the sandy shorelines after the DWH oil spill (OSAT-2 (Operational Science Advisory Team). February 10, 2011). Based on their report, a large amount of deposited oil was detected in the soil samples collected along the shoreline of four oiled sand beaches (Alabama, Florida, Louisiana, Mississippi). The existence of subsurface oil in beaches near the Gulf of Mexico was also noted by other recent studies (Boufadel et al. 2011, Hayworth et al. 2011, Kostka et al. 2011). Subsurface oil has been shown to be a potential hazard to the ecological environment in coastal areas (Culbertson et al. 2008, Lee and Page. 1997, Monson et al. 2011, Peterson et al. 2003).

Biodegradation of oil spilled on beaches has been recognized as an important process in the fate of trapped oil within the beach sediments (Alexander, 1994; Atlas, 1995; Atlas and Hazen, 2011). Studies have demonstrated that indigenous microorganisms can uptake various oil components as sources of carbon and energy for growth and function (Van Hamme et al., 2003; Atlas and Hazen, 2011). The biodegradation depends on the presence of electron acceptors (such as oxygen) and nutrients (such as nitrate/ammonia and phosphate) (Boufadel et al., 1999a; Du et al., 1999; Boufadel et al., 2010). The objective of this study is to predict biodegradation of subsurface oil in a sand beach polluted with the DWH oil spill. The model BIOMARUN, couples a biological Monod kinetic model (Geng et al., 2013) to the transport model MARUN (Boufadel et al.,1999), and was used to simulate the biodegradation of total n-alkanes and polycyclic aromatic hydrocarbons (PAHs) trapped as residual oil in unsaturated zone of a beach in the Gulf of Mexico. The factors limiting the biodegradation of buried oil in the beach include dissolved oxygen (DO) and nitrogen concentrations, salinity, and temperature. Indigenous microbial community with catabolic traits capable of biodegrading oil is commonly present in beaches.

METHOD:

Field setup and measurements

The field study was carried out on a beach located in Bon Secour National Wildlife Refuge, Alabama (Figure 1a). Pore water and sediment samples were collected from the field to measure the concentrations of DO, nitrogen, oil, and microbial biomass that were used as inputs of the oil biodegradation simulations. The beach is primarily composed of uniformly fine- to very fine-grained sand, and is impacted by tide ranging from 0.2 m (neap tide) to 0.8 m (spring tide).

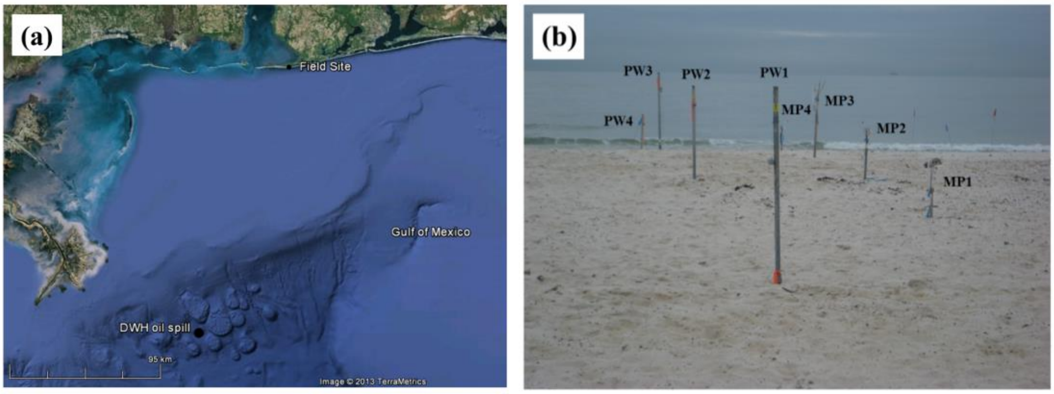


Figure 1: (a) Location of the studied beach on Bon Secour, Alabama (30°14'N, 87°49'W); (b) Site Picture. Four piezometer wells (PW) and four multiport wells (MP) are shown.

Two transects were installed perpendicular to the shoreline in the supratidal zone of the beach (Figure 1b). The distance between the two transects was 2 m. One transect consisted of four stainless steel sampling wells (MP) that were used to collect water samples below the beach surface, and the other transect consisted of four galvanized steel piezometer wells (PW) that were used to measure the groundwater level. Beach topography survey was done using an Electronic Total Station (SET330R3, SOKKIA CO. LTD, Japan). Both transects were almost flat at first, and then extended seaward with an average beach slope of 10% at *x*=15 m (Figure 2a, 2b).

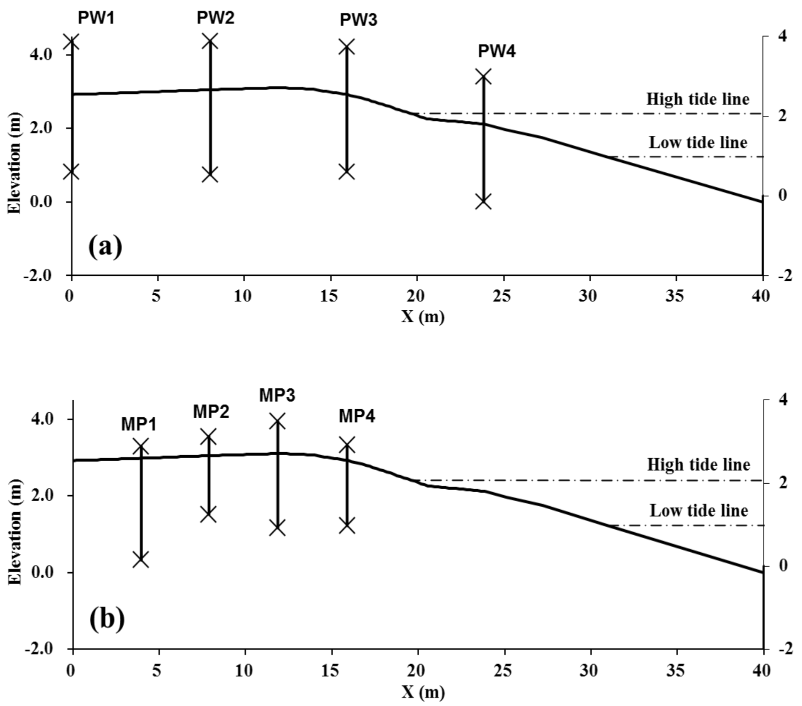


Figure 2: (a) Cross-sectional view of the transect which consisted of four piezometer wells (PW); (b) Cross-sectional view of the transect which consisted of multiport wells (MP).

Pore water samples were collected from the MPs for DO and nitrogen concentration analyses at different times, depending on accessibility (due to tide level) and resources. A Thermo Scientific, RDO optical probe and an ORION 4 Plus hand-held meter (Thermo Scientific, Beverly, MA) were used for DO measurements. The probe was calibrated according to Thermo Scientific Orion Star™ and Star Plus Meter User Guide. Nitrogen concentrations were measured in the lab using an AutoAnalyzer3 (Seal Analytical, Mequon, WI) with colorimetric analysis. Before each set of analysis, a calibration curve was established with R^2 no less than 0.99.

Sediment samples were collected using a stainless steel core sampler that was driven into the sediment using a sliding hammer. The sediment samples were collected from randomly selected nodes of a grid that was centered on each MP. Each core sample was collected in a disposable plastic liner for oil and microbiological analysis. Residual oil concentration and microbial biomass in the samples were measured. The concentrations of n-alkanes and PAHs were measured by SW846 Method 8015 and SW846 Method 8270 SIM, respectively. The abundances of alkane and PAH degraders were determined using 96-well MPN (most probable number) tests. Five µL of filter-sterilized hexadecane were added to each well as carbon source for alkane degraders. PAH-degrader plates were coated with solution consisting of phenanthrene (10 g/L), fluorine (1 g/L), and dibenzothiophene (1 g/L) in pentane before the medium was added. Alkane and PAH degraders were incubated in Bushnell-Hass Broth (Difco Laboratories, Sparks, MD) medium (0.2 g/L of $MgSO_4$; 0.02 g/L of $CaCl_2$; 1.0 g/L KH_2PO_4; 1.0 g/L of $(NH_4)_2HPO_4$; 1.0 g/L of KNO_3; 0.05 g/L of $FeCl_3$). Additionally, yeast extract with concentration of 0.2 g/L was added to the PAH medium to meet nutrient requirements for PAH degraders. The incubation was conducted in the dark at room temperature (23 ± 2 ^oC) and the duration was 2 and 3 weeks for alkane- and PAH-degraders, respectively.

Mathematical model:

A reactive transport model, BIOMARUN, was developed to predict the biodegradation of subsurface oil in porous media. The model couples the biological model, BioB, with the density-dependent groundwater flow and solute transport model, MARUN. The model BIOMARUN relies on the solution of equations for water flow and solute transport to address the biodegradation of organic substrates (up to two compounds). The equation for water flow has been described in previous studies (Boufadel et al., 1999b). Two organics substrates and associated degraders can be considered in the model and expressed as follows.

$$\varphi SR_{Ci}\frac{\partial C_i}{\partial t} = \nabla\cdot(\varphi SD\cdot\nabla C_i) - \mathrm{q}\cdot\nabla C_i + \varphi SR_{Ci}\, r_{Ci},\ i=1,\ 2 \quad (1)$$

Where C_i is the concentration of a species (substrate or substrate degrader), φ is the porosity, S is the soil moisture ratio, q is the Darcy flux vector, D represents the physical dispersion tensor, R_{Ci} is the retardation factor of the species, and r_{ci} is biological reaction rate. Note that C=S denotes substrate and C=X denotes substrate degrader.

There are several kinetics-based models-ranging from those where the kinetics are represented as first-order decay (Venosa et al., 1996; Venosa et al., 2010) to more complicated models where Monod expressions are used (Nicol et al., 1994; Geng et al., 2013) that describe hydrocarbon biodegradation rates. As the latter approach is more general and can reduce to first-order kinetics when the hydrocarbon concentration is small, it was used in this study. The rate of substrate biodegradation, r_{Si}, was considered proportional to biomass growth (Rittman and McCarty, 2001):

$$r_{Si} = -\frac{\mu_i}{Y_{Xi}} X_i \text{, } i\text{=1, 2} \qquad (2)$$

Where μ_i is growth coefficient (day^{-1}); Y_{Xi} is yield coefficient; and X_i is microbial biomass.

The growth rate of the biomass, r_{Xi}, was assumed to be first-order with respect to the biomass concentration (Kindred and Celia, 1989a).

$$r_{Xi} = (\mu_i - k_{di}) X_i \text{, } i\text{ =1, 2} \qquad (3)$$

Where k_{di} is decay constants (day^{-1}). The growth coefficient is limited by the availability of electron acceptor (oxygen), nitrogen, substrate (organic matter), and the field capacity of biomass. It is given herein as a multiplicative Monod formulation:

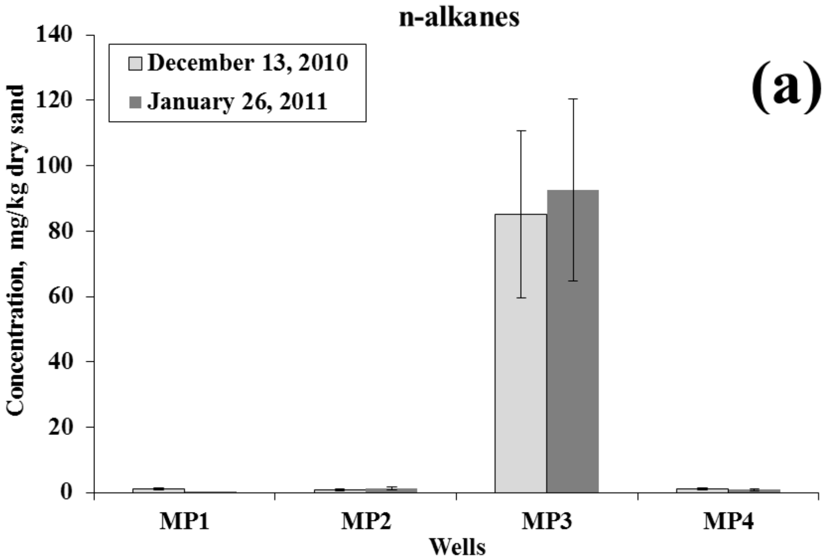
$$\mu_i = \mu_{i\max}\left(1 - \frac{X_i}{X_{i\max}}\right)\left(\frac{S_i}{K_{Si} + S_i}\right)\left(\frac{N}{K_N + N}\right)\left(\frac{O}{K_O + O}\right) \text{, } i\text{=1, 2} \qquad (4)$$

Where $\mu_{i\max}$ is the maximum growth coefficient (day^{-1}); K_S is the half-saturation concentration (mg/kg sand); N is the nitrogen concentration (mg-N/L of pore water); and K_N is the half-saturation concentration for nitrogen consumption (mg-N/L of pore water). It is assumed that the concentration of phosphate is not limiting. In field environments, the size of the microbial population in porous medium is constrained by factors such as pore space, production of inhibitory metabolites, and sloughing of microbial mass (Weise and Rheinheimer, 1977; Kazunga and Aitken, 2000; Rønn et al., 2002). To avoid unreasonably high microbial population, we introduced a term, $(1 - \frac{X}{X_{\max}})$, to the model to account for the decrease in biomass accumulation when the microbial concentration approaches its maximum value. (Kindred and Celia, 1989b; Schirmer et al., 2000).

RESULTS/DISCUSSION:

Field measurements:

Based on the field observation and measurements, the oil-contaminated layer at Bon Secour beach extended from the beach surface to about 0.15 m below the surface but was only detected in the vicinity of MP3. Figure 3 (a-b) shows the measured concentrations of n-alkanes and PAHs. The concentrations of residual oil near MP3 were about 90 mg/kg dry sediment for n-alkanes and 3.5 mg/kg sediment for PAHs. In contrast to the concentrations near MP3, the residual oil in other three MP locations were negligible (≤ 1.14 mg n-alkanes/kg dry sediment; ≤ 0.06 mg PAH/kg dry sediment). The results indicated that the investigated area of the beach was contaminated with oil as residual form, while the heavily oil-contaminated zone was in the vicinity of MP3.



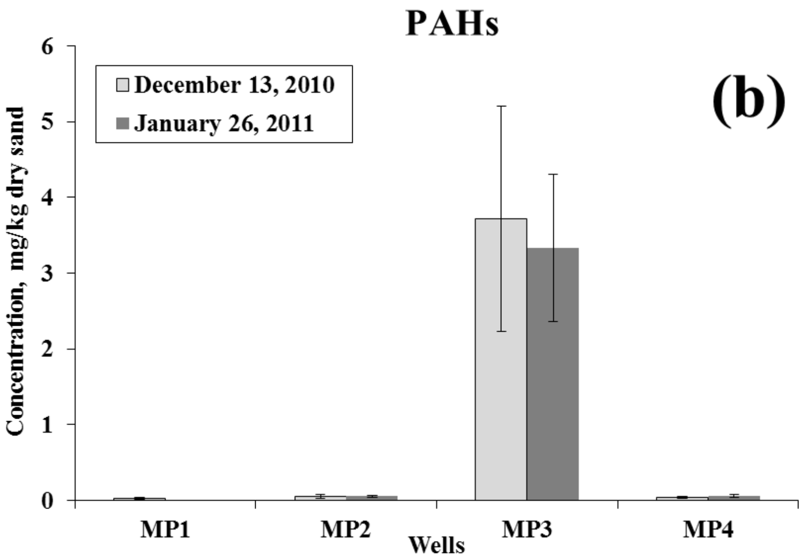


Figure 3 (a-b): Concentrations of n-alkanes (a) and PAHs (b) near MP wells at two different sampling events (error bars represent ± one standard deviation unit).

Figure 4 (a-b) shows the population of n-alkane- and PAH- degraders in all sampling events. The population of n-alkane- and PAH- degraders near MP3 was higher than that near the other three MP wells, which implies greater microbial activities near the heavily oil-contaminated area. The temporal variation of microbial population did not show a clear trend at all the wells. This probably occurred because many other factors (e.g., temperature, available interfacial area, and soil moisture) besides oil concentration impact subsurface microbial activity (Vaughan, 1985; Zhou and Crawford, 1995; Geng et al., 2013).

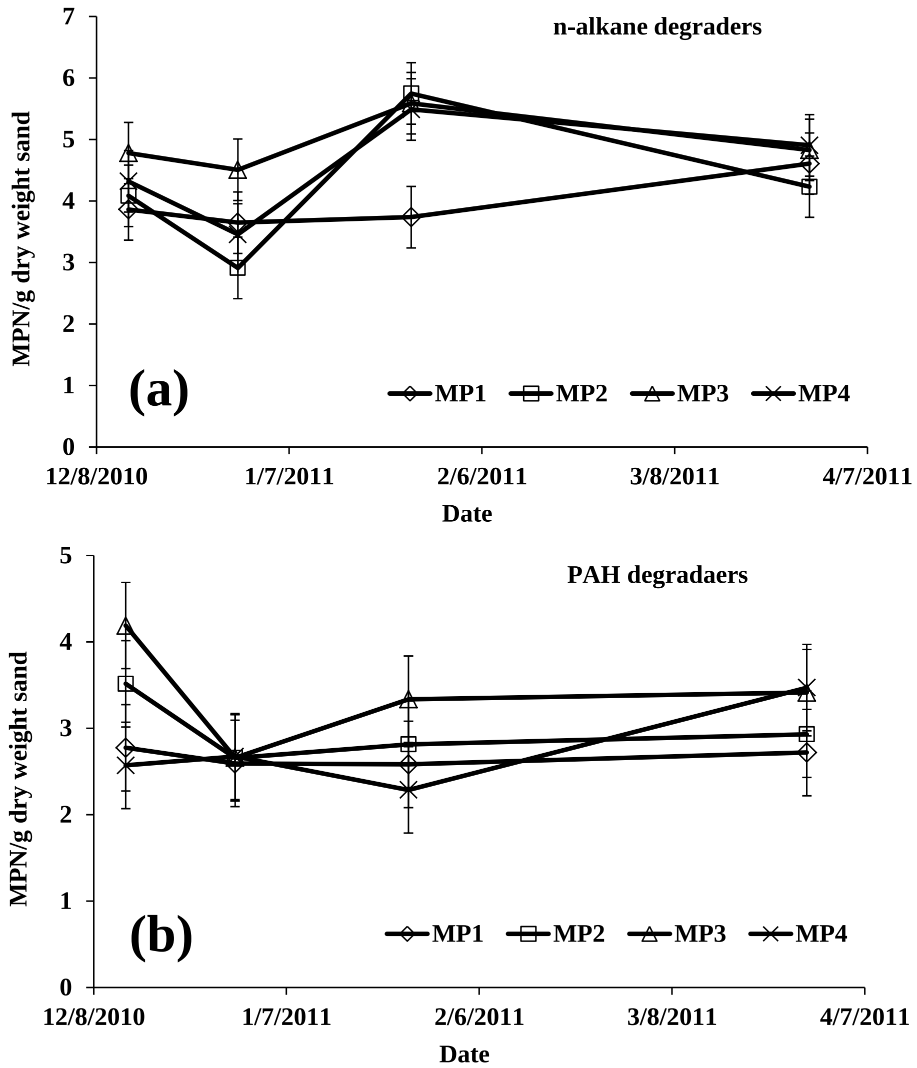


Figure 4 (a-b): Growth of n-alkane degraders (a) and PAH degraders (b) at MP locations (error bars represent ± one standard deviation unit).

Table 1 shows nitrogen concentration (nitrite + nitrate) and DO measured in MP wells. The average nitrogen concentration at each MP well was about 1.25 mg/L. Many studies have reported that the optimal range of nitrogen concentration for oil biodegradation is from 2.0 mg/L to 10.0 mg/L (Boufadel et al., 1999a; Du et al., 1999). Therefore, nitrogen was limited for oil biodegradation in this oil-contaminated beach. The DO concentration measured in the field at different MP wells were between 7.4 mg/L and 9.1 mg/L. This range meets the critical oxygen level (2.0 mg/L) above which aerobic oil biodegradation can be sufficiently supported (Chiang et al., 1989; Michaelsen et al., 1992).

Table 1. Summary of Nitrate + Nitrite Concentration and DO from MP wells.

	Nitrite + Nitrate (Mean ± SD), mg N/L	DO (Mean ± SD), mg/L
MP1	1.1±0.8	7.8±1.6
MP2	0.9±1.0	9.1±0.15
MP3	1.6±1.1	7.6±0.87
MP4	1.4±1.0	7.4±1.03
Seawater	0.2±0.1	8.0±0.2

Modeling results:

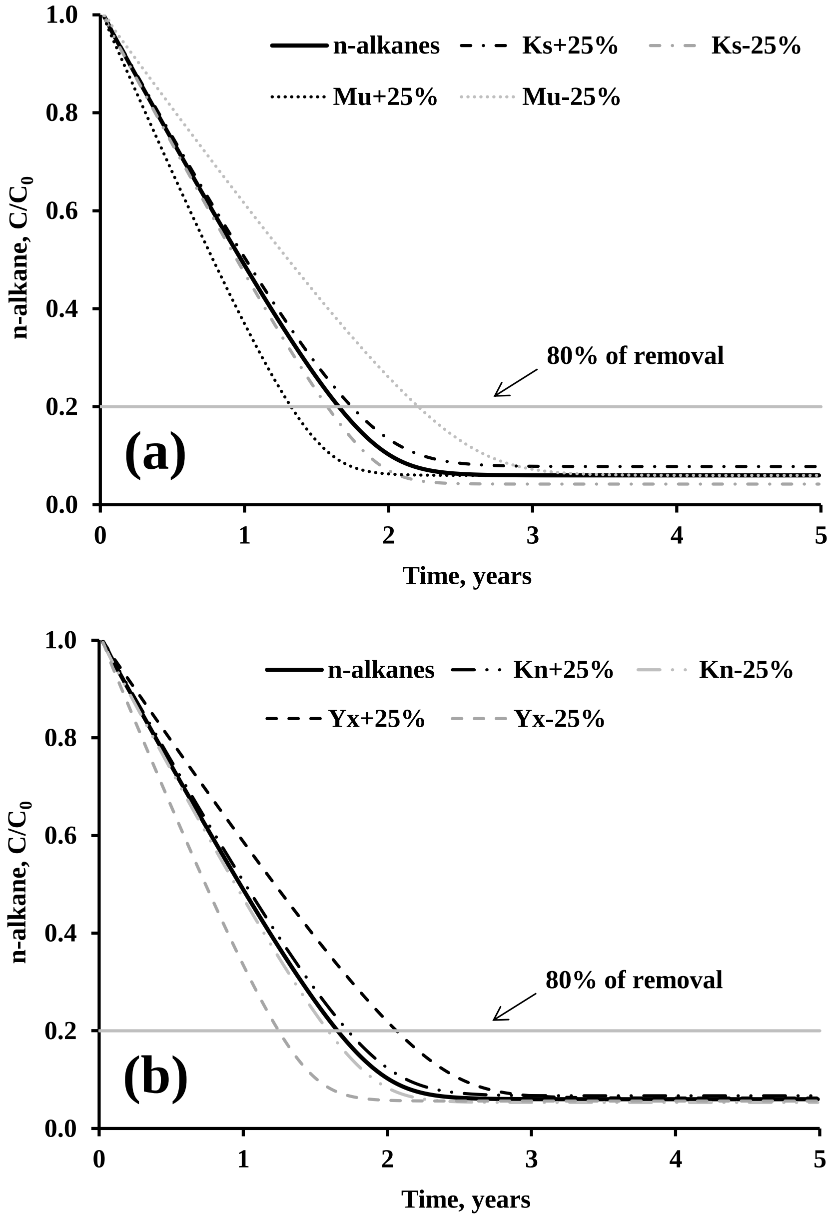
As the oil was trapped as residual form in the unsaturated zone of the beach, we used only the biodegradation module of BIOMARUN (i.e., BIOB) for simplicity. Transport of solute was not considered for this particular work. The concentration of oxygen was assumed to be large enough as to not limit biodegradation. The concentration of nitrogen was taken as constant equal to the measured value in the field (Table 1). The effect of temperature and salinity on inhibition on oil biodegradation was not considered in this work, but will be accounted for in future.

Figure 5 shows the simulation results of n-alkanes and aromatics biodegradation using BIOMARUN. The values of parameter used in the simulation were based on the literature (Table 2). Note that the concentrations are normalized by C_0, which is the average of the oil concentrations measured in December 2010 and January 2011. The values for the kinetic parameters have been reported in a large range under different aerobic conditions. For example, the values of kinetic parameters used in Nicol et al. (1994) were for oil biodegradation in saturated porous medium, while in our study the residual oil was in a variably-saturated zone of the beach. For this reason, the sensitivity of model prediction to the parameters was conducted by varying the value of each parameter ± 25%. Simulation results indicated that n-alkanes and PAHs would be biodegraded by 80% after 2 ± 0.5 years and 3.5 ± 0.5 years, respectively. These results are similar to the estimation by a previous study (Mortazavi et al., 2013). They investigated the rates of crude oil degradation by the extant microorganisms in intertidal sediments from a northern Gulf of Mexico beach. Their results suggested that the oil would be biodegraded by 80% within 1.5 years.

Table 2. Parameter values used in BIOMARUN

Parameters	Literature Value[a]
Maximum growth rate for n-alkane degraders (day^{-1})	7.6
Maximum growth rate for PAH degraders (day^{-1})	1.6
Yield coefficient for n-alkane degraders	1.1
Yield coefficient for PAH degraders	1.1
Half-saturation concentration for n-alkanes (mg/kg sediment)	25
Half-saturation concentration for PAHs (mg/kg sediment)	25
Endogenous biomass decay rate (day^{-1}) for n-alkanes	0.1
Endogenous biomass decay rate (day^{-1}) for PAHs	0.01
Half-saturation constant of nitrogen (mg/L) for n-alkanes	0.45
Half-saturation constant of nitrogen (mg/L) for PAHs	0.45
Initial concentration of n-alkane degrader (mg/kg dry sediment)	0.2
Initial concentration of PAH degrader (mg/kg dry sediment)	0.02

[a]Literature values were used from Nicol et al. (1994)


n-alkanes
Ks+25%
Ks-25%
Mu+25%
Mu-25%
80% of removal
(a)
n-alkane, C/C0
Time, years
1.0
0.8
0.6
0.4
0.2
0.0
0
1
2
3
4
5
n-alkanes
Kn+25%
Kn-25%
Yx+25%
Yx-25%
80% of removal
(b)
n-alkane, C/C0
Time, years

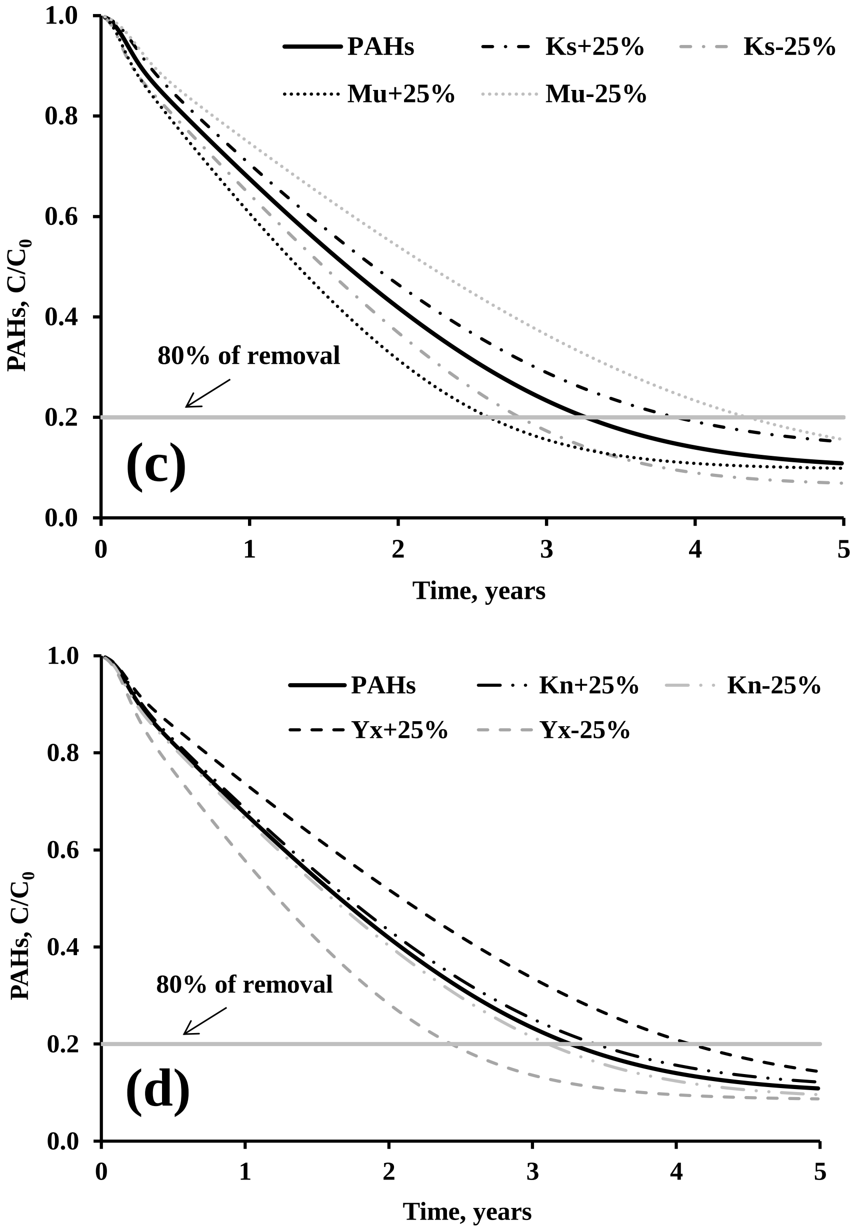


Figure 5 (a-d): The variation of normalized concentration of n-alkanes (a-b) and PAH (c-d) as a function of time.

SUMMARY AND CONCLUSION:

A combined field and modeling study was conducted to investigate the biodegradation of subsurface oil in a sandy beach contaminated with the DWH oil spill. Pore water chemistry results suggested that nitrogen is the limiting factor for the oil biodegradation in the studied beach, while dissolved oxygen concentration is at a sufficient level. The numerical model, BIOMARUN, was used to predict the oil biodegradation. The simulation results indicated that n-alkanes and PAHs would be biodegraded by 80% after 2 ± 0.5 years and 3.5 ± 0.5 years, respectively. The study aims to provide an operational tool to spill responders who need to evaluate specific response alternatives in real time.

REFERENCES:

Alexander, M., 1994. Biodegradation and bioremediation. Academic Press Inc.

Atlas, R.M., 1995. Petroleum biodegradation and oil spill bioremediation. Marine Pollution Bulletin, 31(4): 178-182.

Atlas, R.M. and Hazen, T.C., 2011. Oil biodegradation and bioremediation: a tale of the two worst spills in U.S. History. Enviromental Science and Technology, 45(16): 6709-6715.

Boufadel, M.C. et al., 1999a. Optimal nitrate concentration for the biodegradation of n-heptadecane in a variably-saturated sand column. Environmental Technology, 20(2): 191-199.

Boufadel, M.C., Sharifi, Y., Van Aken, B., Wrenn, B.A. and Lee, K., 2010. Nutrient and Oxygen Concentrations within the Sediments of an Alaskan Beach Polluted with the Exxon Valdez Oil Spill. Environmental Science & Technology, 44(19): 7418-7424.

Boufadel, M.C., Suidan, M.T. and D, V.A., 1999b. A numerical model for density-and-viscosity-dependent flows in two- dimensional variably-saturated porous media. Journal of Contaminant Hydrology, 37: 1-20.

Chiang, C.Y., Salanitro, J.P., Chai, E.Y., Colthart, J.D. and Klein, C.L., 1989. Aerobic Biodegradation of Benzene, Toluene, and Xylene in a Sandy Aquifer - Data-Analysis and Computer Modeling. Ground Water, 27(6): 823-834.

Du, X. et al., 1999. Optimal nitrate concentration supporting maximum crude oil biodegradation in microcosms. Proceedings of 1999 International oil Spill Conference.

Geng, X., Boufadel, M.C. and Wrenn, B., 2013. Mathematical modeling of the biodegradation of residual hydrocarbon in a variably-saturated sand column. Biodegradation, 24(2): 153-163.

Kazunga, C. and Aitken, M.D., 2000. Products from the incomplete metabolism of pyrene by polycyclic aromatic hydrocarbon-degrading bacteria. Applied and Environmental Microbiology, 66(5): 1917-1922.

Kindred, J.S. and Celia, M.A., 1989a. Contaminant Transport and Biodegradation .2. Conceptual-Model and Test Simulations. Water Resources Research, 25(6): 1149-1159.

Kindred, J.S. and Celia, M.A., 1989b. Contaminant transport and biodegradation: 2. Conceptual model and test simulations. Water Resources Research, 25(6): 1149-1159.

Michaelsen, M., Hulsch, R., Hopner, T. and Berthecorti, L., 1992. Hexadecane Mineralization in Oxygen-Controlled Sediment-Seawater Cultivations with Autochthonous Microorganisms. Applied and Environmental Microbiology, 58(9): 3072-3077.

Mortazavi, B., Horel, A., Beazley, M.J. and Sobecky, P.A., 2013. Intrinsic rates of petroleum hydrocarbon biodegradation in Gulf of Mexico intertidal sandy sediments and its enhancement by organic substrates. Journal of hazardous materials, 244: 537-544.

Nicol, J.P., Wise, W.R., Molz, F.J. and Benefield, L.D., 1994. Modeling biodegradation of residual petroleum in a saturated porous column. Water Resour. Res., 30: 3313-3325.

Rittman, B.E. and McCarty, P.L., 2001. Environmental Biotechnology: Principles and Applications. McGraw Hill, Columbus, Ohio.

Rønn, R., McCaig, A.E., Griffiths, B.S. and Prosser, J.I., 2002. Impact of protozoan grazing on bacterial community structure in soil microcosms. Applied and Environmental Microbiology, 68(12): 6094-6105.

Schirmer, M., Molson, J.W., Frind, E.O. and Barker, J.F., 2000. Biodegradation modelling of a dissolved gasoline plume applying independent laboratory and field parameters. Journal of Contaminant Hydrology, 46(3-4): 339-374.

Van Hamme, J.D., Singh, A. and Ward, O.P., 2003. Recent advances in petroleum microbiology. Microbiology and Molecular Biology Reviews, 67(4): 503-549.

Vaughan, D., 1985. Soil organic matter and biological activity, 16. Springer.

Venosa, A.D., Campo, P. and Suidan, M.T., 2010. Biodegradability of Lingering Crude Oil 19 Years after the Exxon Valdez Oil Spill. Environmental Science & Technology, 44(19): 7613-7621.

Venosa, A.D. et al., 1996. Bioremediation of an experimental oil spill on the shoreline of Delaware Bay. Enviromental Science and Technology, 30: 1764-1775.

Weise, W. and Rheinheimer, G., 1977. Scanning electron microscopy and epifluorescence investigation of bacterial colonization of marine sand sediments. Microbial Ecology, 4(3): 175-188.

Zhou, E. and Crawford, R.L., 1995. Effects of oxygen, nitrogen, and temperature on gasoline biodegradation in soil. Biodegradation, 6(2): 127-140.