OPERATIONAL SCIENCE ADVISORY TEAM

SUMMARY REPORT FOR FATE AND EFFECTS OF REMNANT OIL REMAINING IN THE BEACH ENVIRONMENT

Annex E: Biodegradation Assessment Tool (BIOMARUN)

Executive Summary

Oil from the Deepwater Horizon (DWH) spill is buried in the supratidal zones (landward of the high tide line) of beaches of the Gulf of Mexico. The oil is approximately 0.30 m (1 foot) deep, and is above the water table in the vadose zone (or the unsaturated zone). An illustration of the oil entrapment in the vadose zone is shown in Figure 1. The biodegradation of this oil could occur provided there is sufficient soil moisture (i.e., pore water) and that the concentration of oxygen and nutrients are not too low to be limiting (Bragg et al., 1994; Venosa et al., 1996; Boufadel et al., 1999; Du et al., 1999).

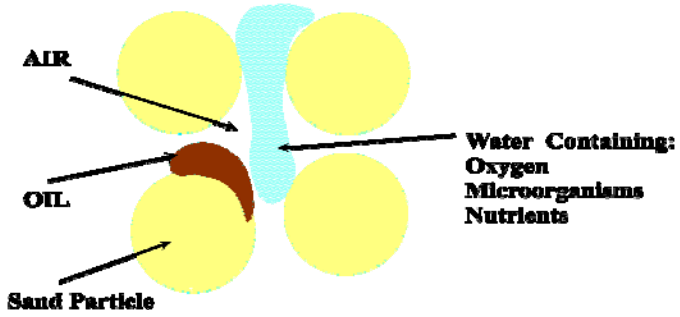

Figure 1: Illustration of buried oil in the supratidal area (landward of the high tide line) in the vadose zone (i.e., above the water table) of beaches.

The goal of the project was to predict the biodegradation rate of oil buried in the supratidal zones of beaches. The project relied on field measurements made at three sites (Bon Secour, Alabama; Fort Pickens, Florida; and Grand Isle; Louisiana) and computer simulations using the BIOMARUN model (Appendix) based on these measurements. The field properties that were measured included: water level, water temperature, salinity, nutrient concentration, dissolved oxygen, sulfate concentration, and microbial density.

The simulations were for the biodegradation of long chain alkanes (C30) and polycyclic aromatic hydrocarbons, PAHs, (3 to 4 rings). Environmental properties were measured in the field and used as input to the model. These properties included the following: oil concentration within the sediments, porosity of sediments, permeability of sediments, soil moisture, salinity, nutrient concentration, oxygen concentration, and sulfate concentration. For example, at Bon Secour and

Fort Pickens, the soil moisture surrounding the oil was about 20 to 30% of the porosity, while at Grand Isle, soil moisture was more than 90%. In all cases, the water table was below the entrapped oil; the water table was about 1 m (3 feet) below the oil at Bon Secour and Fort Pickens and about 0.3 m (1 foot) below the oil at Grand Isle.

Figures 2 through 4 show the normalized concentration of alkanes and PAHs as a function of time at Bon Secour, Fort Pickens, and Grand Isle, respectively. The concentrations were normalized by the values from sediments obtained in mid-December 2010. Time zero in these figures is July 2010.

Figure 2 (Bon Secour) shows that the concentration of alkanes reaches 13% of the initial value at 2.5 years, and that the degradation is very slow beyond that time. The PAH concentration decreased slower than that of the alkanes reaching 15% of the initial value at 5 years. The model showed that not much degradation occurs after 5 years (not shown in figure 2 for brevity). Due to uncertainty in the estimated model parameters, the times provided are accurate within 50%. This means that the decrease of the alkanes concentration to 13% should be viewed as occurring at 2.5 years ± 1.25 years. Similarly the decrease of the PAHs to 15% should be viewed as occurring at 5.0 years ± 2.5 years.

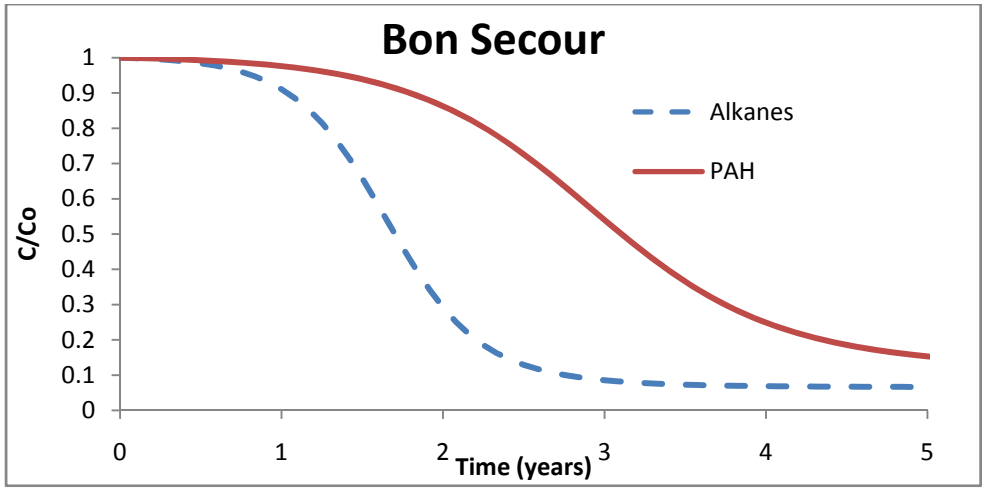

Figure 2: Predicted concentration with time at Bon Secour (AL). Time zero is July 2010.

Figure 3 (Fort Pickins) shows that the concentration of alkanes reaches 15% of the initial value at 2.5 years, and that the degradation is very slow beyond that time. The PAH concentration decreased slower than that of the alkanes, reaching 20% of the initial value at 5 years. The model showed that not much degradation occurs after 5 years (not shown in figure 3 for brevity). Similar to the discussion on uncertainty above (for Bon Secour), the times provided are accurate within 50%. This means that the decrease to 15% of the alkanes concentration should be viewed as occurring at 2.5 years ± 1.25 years. Similarly the decrease of the PAHs to 20% should be viewed as occurring at 5.0 years ± 2.5 years.

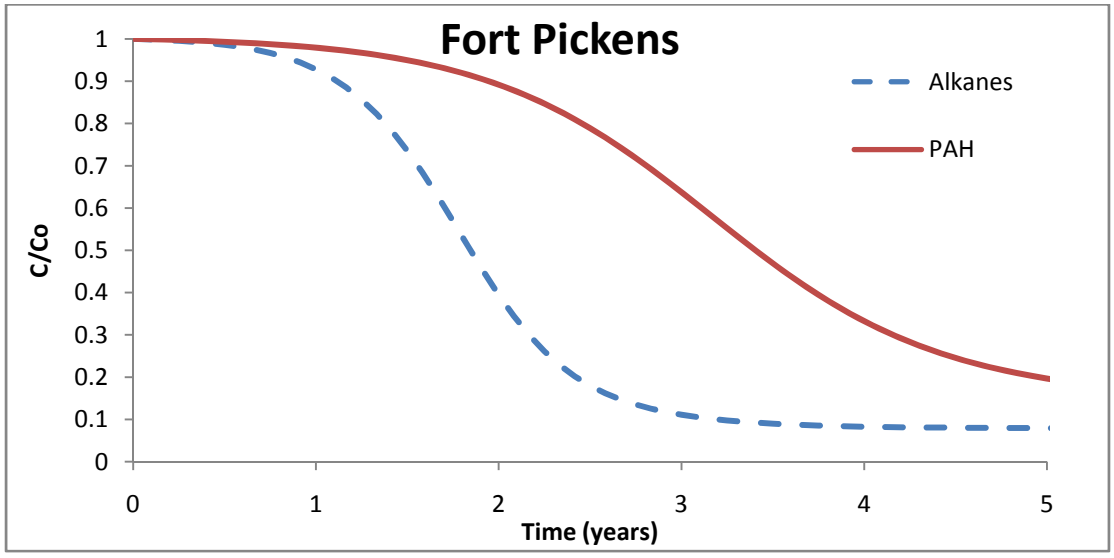

Figure 3: Predicted concentration with time at Fort Pickens (FL). Time zero is July 2010.

Figure 4 (Grand Isle) shows that the concentration of alkanes reaches about 80% of the initial value at 5 years, and the degradation continues at a slow rate causing the concentration to reach 50% of the initial value at 10 years. The concentration of PAHs at 5 years is about 95% of the initial value, and decreases at a very slow rate until reaching 87% at 10 years.

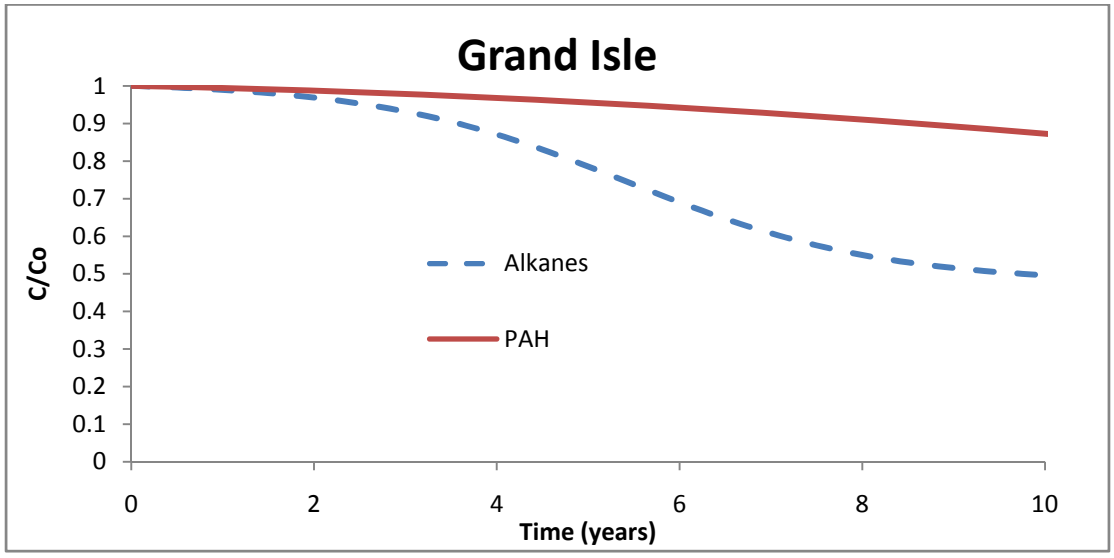

Figure 4: Predicted concentration with time at Grand Isle (LA). Time zero is July 2010.

The comparable biodegradation of oil at Bon Secour and Fort Pickens indicates that the overall conditions at these sites are similar. The soil moisture at oiled zones was measured at 20% and 30% of the porosity at Bon Secour and Fort Pickens, respectively. Thus, all factors being equal, the biodegradation at Fort Pickens is expected to be faster. However, the nutrient concentration

was 1.2 mg-N/L and 0.80 mg-N/L at oiled zones at Bon Secour and Fort Pickens, respectively. Thus, the higher nutrient concentration at Bon Secour results in higher biodegradation rates (all factors being equal). For this reason, the biodegradation of oil at Bon Secour and Fort Pickens was found to be comparable.

The beach at Grand Isle had a very low oxygen concentration (about 0.4 mg/L) indicating that aerobic biodegradation of oil is essentially not occurring. The smell of hydrogen sulfide (rotten eggs) while excavating the sediments suggested that sulfate reduction was occurring, which was confirmed with detailed environmental measurements. Therefore, the biodegradation of oil could be occurring during sulfate reduction (i.e., the sulfate plays a similar role to oxygen). However, the rate of oil biodegradation during sulfate reduction is usually around 20% that of aerobic oil biodegradation, which explains the slow biodegradation of the alkanes and PAHs (shown in Figure 4). The high soil moisture at the site (90% of the porosity) and the high nutrient concentration (2.0 mg-N/L) could not compensate for the severe deficiency of oxygen at Grand Isle.

RATIONALE OF THE MODELING

A major assumption was made related to the hydraulics in the beaches. While the BIOMARUN model can simulate the movement of water and chemicals in the beaches, we found after conducting simulations, that prediction of the environmental conditions for the following 5 years would require detailed forecasting of hydrology, which is not available for these sites. For this reason, we considered the present conditions to persist, and as such, there was no need to model water movement and chemical transport in the pore water. In other words, we used only the biodegradation module of the code BIOMARUN.

The parameter values for the biological module of BIOMARUN are reported in Table 1 along with their respective comparisons with the literature. The concentrations used in the simulations are reported in Table 2, and we explain our selection of these parameters herein. For both Bon Secour and Fort Pickins, we used the oxygen concentration measured in the water below the oil, which was approximately 8.2 mg/L, which is close to the solubility limit of oxygen in water in contact with air. This value was used in the simulation because the pore water in the vadose zone is in direct contact with air. For Bon Secour and Fort Pickins, we measured nutrient concentrations of 1.2 mg-N/L and 0.8 mg-N/L, respectively. However, the nutrient concentration (nitrogen) used in the biological module was half the measured values, because the nutrients are expected to become depleted during oil biodegradation and the replenishment is not as continuous as for oxygen. The replenishment of nitrogen would occur due to rain whose concentration is 0.8 mg-N/L or by wave splash whose concentration is 0.2 mg-N/L. In that regard, the constant concentrations of 0.6 mg-N/L and 0.4 mg-N/L for Bon Secour and Fort Pickens, respectively, are reasonable.

The beach at Grand Isle had a very low oxygen concentration (around 0.4 mg/L) suggesting that aerobic biodegradation of oil is very slow. Therefore, the biodegradation of oil could be occurring during sulfate reduction (i.e., the sulfate plays a similar role to oxygen). However, the rate of oil biodegradation during sulfate reduction is usually small, less than 20% that of aerobic oil biodegradation. To reduce the rate to 20% of the aerobic condition, we used an oxygen concentration of 1.0 mg/L, and by doing so the maximum rate was multiplied by 0.2. We used the measured nutrient concentration of 2.0 mg-N/L. This rate should be viewed as an upper limit on the actual biodegradation rate.

Microbial counts were obtained using MPN (most probable number), and we found that the microbial count of alkane and PAH degraders at oiled locations was, on the average, 10 fold the values at unoiled areas. Thus, to run the model, we used the microbial count at unoiled areas as the initial condition for the simulation, assumed to occur in July 2010 when the oil made contact with the shorelines. The simulations at Bon Secour and Fort Pickens gave biomass values comparable to what was measured in December 2010 at oiled areas on the three beaches. This finding indicates that the model was able to capture the increase in hydrocarbon degraders within the 6 months duration.

Table 1: Model parameter values for F1 (long chain and branched alkanes) and F2 (PAH)

Parameter	Value	Literature values
K_O, Oxygen ½ sat constant	2.0 mg/L	(1) below
K_N, Nitrogen ½ sat constant	0.50 mg/L	(2) below
Porosity, ϕ	0.35 (Bon Secour) 0.35 (Fort Pickins) 0.35 (Grand Isle)	(3) below
Soil Moisture, θ	0.07 (Bon Secour) 0.11 (Fort Pickins) 0.32 (Grand Isle)	S*ϕ, where S was measured S=0.2 Bon Secour S=0.3 Fort Pickins S=0.9, Grand Isle
Optimum Soil Moisture, θ_m	0.28 (Bon Secour) 0.28 (Fort Pickins) 0.28 (Grand Isle)	0.8*porosity
μ_{max1}(Alkane degraders)	0.15 day^{-1}	0.2 day^{-1}, Venosa et al. (1996)
k_{d1}	0.05 μ_{max1}	0.05 μ_{max1}: Nicole et al. (1994)
y_{X1}, yield coefficient	0.76 g biomass/g of C	Average of literature Nicole et al. (1994) Essaid et al. (1995)
K_{F1}, Food ½ sat constant	50.0 mg/L of F1	Empirical
μ_{max2}	0.10 day^{-1}	0.13 day^{-1}, Venosa et al. (1996)
k_{d2}	0.05 μ_{max2}	0.05 μ_{max2}: Nicole et al. (1994)
Y_{X2}, yield coefficient	0.76 g biomass/g of C	Average of literature Grady and Lim (1980)
K_{F2}, Food ½ sat constant	50.0 mg/L of F2	Empirical

(1) Nutrient limitation appears when the nutrient concentration reaches 2.0-5.0 mg-N/L. For this reason, we select a half rate constant of 0.50 mg-N/L.
(2) The porosity in the laboratory of all beaches was measured at around 0.40. We assumed that beaches were more compacted in the field, and for this reason we set the field porosity at 0.35. Most likely, the field porosity at Grand Isle is close to what is observed in the laboratory due to the fine texture of the sediment. However, considering the uncertainty in other parameters, it is realistic to assume a porosity of 0.35 for all sites.

Table 2: Concentrations used in the model simulation

Alkanes	2.0 mg/kg of dry sediments (Fort Pickens) (1)
PAH	1.5 mg/kg of dry sediments (Fort Pickens) (1)
Initial concentration of alkane degraders	0.050 mg/L, Approximate based on MPN data farthest from oil location.
Initial concentration of PAH degraders	0.050 mg/L, Approximate based on MPN data farthest from oil location.
Oxygen (Constant value closest to oil)	8.1 mg/L Bon Secour 8.3 mg/L Fort Pickens 0.4 mg/L (But sulfate reduction is assumed)
Nitrogen (Constant value average of the whole beach)	Bon Secour: 0.60 mg/L (Half the field value of 1.20 mg/L) Fort Pickens:0.40 mg/L (Half the field value of 0.80 mg/L) Grand Isle: 2.0 mg/L (Equal to the field value of 2.0 mg/L due to replenishment from inundation)

(1) The Fort Pickens oiling data were considered as representative of other sites, as the oiling data of other sites were not available at the time of the report.

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Biodegradation Assessment Tool

Appendix A

BIOMARUN
MODEL DESCRIPTION

The BIOMARUN model is a fate and transport model that simulates the biodegradation of two organic compounds in the subsurface of beaches and aquifers. The model can simulate the biodegradation of oil located both below and above the water table, and as such is directly applicable to oil in tidally influenced beaches, in particular the Deepwater Horizon (DWH) oil buried in some of the beaches of the Gulf of Mexico.

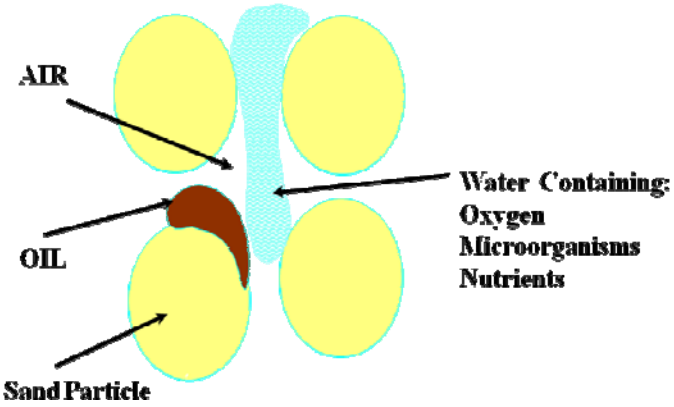

Figure 1: Illustration of buried oil in the vadose zone of beaches. As the pores are not completely filled with water (due the presence of air), one use the “unsaturated zone” descriptor for that portion of the beach.

The model BIOMARUN has three main modules: Water flow, solute transport, and biodegradation (Figure 2). The first two modules are the components of MARUN (for marine unsaturated, Boufadel et al., 1999). The MARUN model accounts for the effects of water salinity on water density and viscosity, and subsequently on water motion (heavier water tends to sink when surrounded by lighter water). More documentation on the first two modules of BIOMARUN can be found in Boufadel et al., (1999), Boufadel (2000), Li and Boufadel (2010), and Xia et al., (2010).

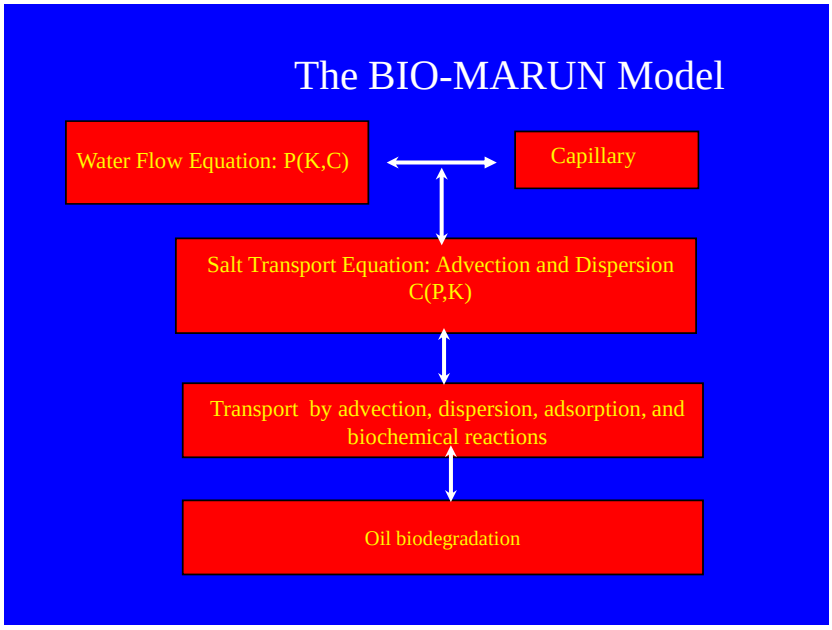

Figure 2: Modules of the BIOMARUN model.

Biodegradation Module

The biodegradation module assumes that there are two types of foods: F1 and F2. In this application F1 is the long chain alkanes and F2 is the polycyclic aromatic hydrocarbons (PAH). Each food gets consumed by a group of micro-organisms, X1 and X2. The growth of these microorganisms (or biomass) is modeled numerically according to the equations:

$$X_{1,n+1} = X_{1,n} \exp[(\mu_1 - k_{d1})\Delta t] \quad (1a)$$

$$X_{2,n+1} = X_{2,n} \exp[(\mu_2 - k_{d2})\Delta t] \quad (1b)$$

$X_{1,n+1}$ and $X_{2,n+1}$ are the concentrations of biomass at time level "n+1" and $X_{1,n}$ and $X_{2,n}$ are the concentration of biomass at time step "n". The parameter k_{d1} is a decay coefficient that accounts for microbial death (1/day). The coefficients μ_1 and μ_2 are known as the growth coefficients. Assuming a multiplicative Monod, they are given herein as:

$$\mu_1 = \frac{\mu_{1\max}}{I_\theta}\left(\frac{N}{K_N + N}\right)\left(\frac{O^4}{K_O + O^4}\right)\left(\frac{F_1}{K_{F1} + F_1}\right) \quad (2a)$$

$$\mu_2 = \frac{\mu_{2\max}}{I_\theta}\left(\frac{N}{K_N + N}\right)\left(\frac{O^4}{K_O + O^4}\right)\left(\frac{F_2}{K_{F2} + F_2}\right) \quad (2b)$$

Where $\mu_{1\max}$ and $\mu_{2\max}$ are the maximum growth coefficient (e.g,. 1/day). The terms of the equations have the following designation: N, nutrient concentration (mg-N/L); O, oxygen concentration (mg/L); F_1, food (mg/L of pore water). The terms K_N, K_o, and K_{F1} are constants. The coefficient I_θ accounts for moisture inhibition (discussed below). For the nutrients and hydrocarbons, the standard Monod is used, as supported by the literature (Nicole et al. 1994; Essaid et al., 1995). However, a modified Monod is used to account for oxygen effects, as shown in Eq. 2.

The fraction $\left(\frac{O^4}{K_O + O^4}\right)$ means that if there is no oxygen (O=0.0 mg/L) then no growth would occur, which is correct. As the oxygen concentration increases, the growth rate increases until reaching a plateau. This is reasonable, as other factors would become limiting for growth, and it is not realistic to increase the growth rate indefinitely by increasing the oxygen concentration. Oxygen limitation appears when the oxygen concentration drops below 2.0 mg/L, and it becomes obvious at 1.0 mg/L and lower (Boufadel et al., 2010). Therefore, we adopted the empirical model reported in Figure 3, which is a modification of the Monod model. The constant K_o is taken as 2.0 $(mg/L)^4$. The traditional Monod model cannot account for the sudden decrease in the aerobic rate when the oxygen concentration drops below 1.0 mg/L. Alternately, when the Monod rate is small at concentration less than 1.0 mg/L then it gives small rates at oxygen concentrations larger than 2.0 mg/L, which is not realistic.

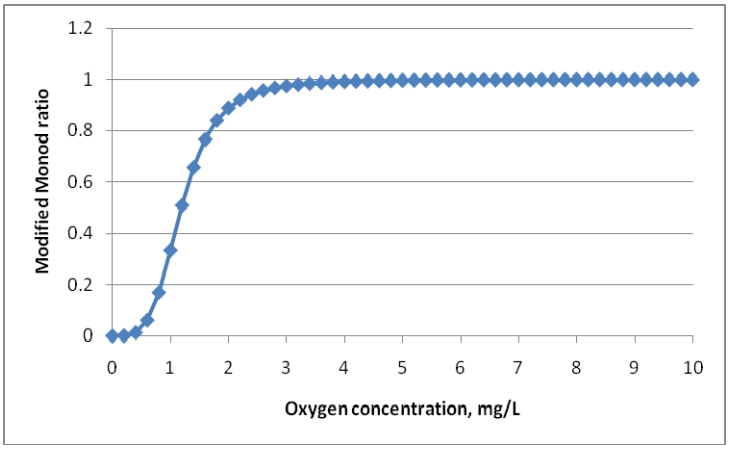

Figure 3: Expression for oxygen effects used in BIOMARUN.

The coefficient I_θ accounts for the effect of soil moisture, which is known to affect microbial activity (Pramer and Bartha, 1972). I_θ is given by the following expression (El-Kadi, 2001):

$$I_\theta = a_\theta - (a_\theta - 1)\exp\left[-\frac{(\theta-\theta_m)^2}{2\sigma_\theta^2}\right] \quad (3)$$

Where θ is the water content, which varies between the residual water content θ_r and the porosity ϕ, and θ_m is the optimal value of the water content for bacterial growth, σ_θ is a parameter of the distribution, and a_θ is the maximum inhibition value. The following values for θ_m, σ_θ, and a_θ were used by El-Kadi [2001]: $\theta_m = 0.228$, $\sigma_\theta = 0.1$, $a_\theta = 5.0$ where the porosity was ϕ=0.4 while the lowest soil moisture was θ_r=0.1. We believe the transition needs to be more gradual, as a study by Fallgren et al. (2010) showed that the microbial activity at 30% saturation is even higher than that at 80%, and for this reason we adopt the value $\sigma_\theta = 0.3$. The resulting function I_θ is plotted in Figure 4. Note that we are assuming that the inhibition behavior is the same for both alkane and PAH degraders, X1 and X2, respectively, which is reasonable considering the uncertainty in the inhibition function.

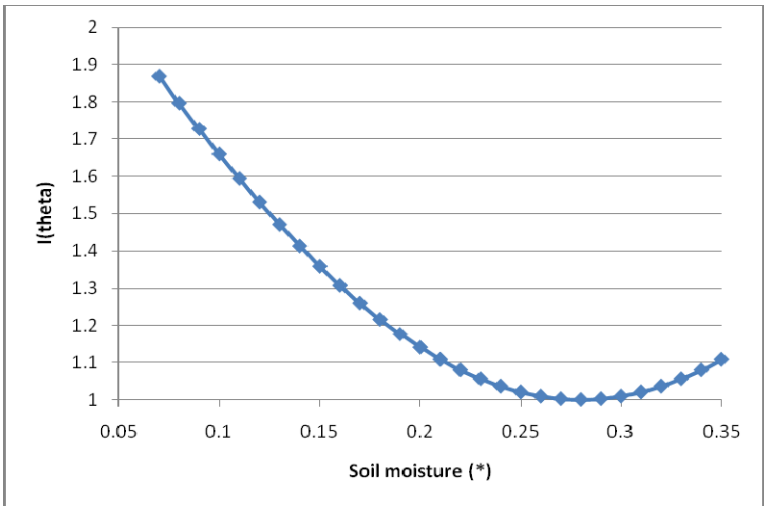

Figure 4: Inhibition parameter as a function of soil moisture for all sites. The optimum is at the soil moisture 0.28 which is 0.80 of the porosity (0.35). A large value of the function I(θ) reflects large inhibition. At low moisture content, not enough "wetting" of the biomass is occurring and inhibition occurs. At high soil moisture, the oxygen tends to become depleted resulting in inhibition. Inhibition

at high soil moisture is much less than inhibition at low soil moisture.

Modeling the Residual Oil

It is common to report the concentration of oil as mg/kg of sediments. For this reason, BIOMARUN converts the concentrations from mg/kg in the given to mg/L to be used within BIOMARUN, then converts them back to mg/kg in the output. To prevent the model from moving oil with water flow, we assigned a large retardation coefficient for the oil concentration (R=1,000).

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