OPERATIONAL SCIENCE ADVISORY TEAM

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

Annex D: SEAM-3D Model

MODELING THE FATE AND TRANSPORT OF POLYAROMATIC HYDROCARBONS IN THE SATURATED ZONE, GRAND ISLE, LOUISIANA

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Executive Summary

A numerical modeling approach was used to assess polyaromatic hydrocarbon (PAH) transport by flowing groundwater in subsurface environments such as those characteristic of Grand Isle, Louisiana. The results of these modeling simulations indicate that because of the low solubility, high sorptive capacity, and relative biodegradability of 2-ring and 3-ring PAHs, these compounds are not expected to be transported long distances (i.e. < 2 meters) from oil masses by flowing groundwater. This limited transport, in turn, will tend to minimize plant and animal exposure to potentially toxic PAH compounds distant from buried non-aqueous phase liquid (NAPL) masses.

Introduction

Defining the Problem

During the spring and summer of 2010, oil from the Deepwater Horizon blowout formed slicks in the Gulf of Mexico and approached shorelines in the states of Louisiana, Mississippi, Alabama, and Florida. In Louisiana, storm surges deposited some of this oil above the high-tide line on several barrier islands including Grand Isle. Downward migration of oil into sandy beach sediments delivered some of this oil to the saturated groundwater systems underlying Grand Isle. This occurrence raises an important question about the environmental fate of the buried oil: Will toxic polyaromatic hydrocarbons (PAHs) associated with the oil leach into groundwater and be transported significant distances? A numerical modeling approach was used to address this question.

Modeling Approach

The dissolution and biodegradation of residual oil depend upon physical, chemical, and biological processes. These processes can be simulated using equations describing mass balance

and mass transfer. This, in turn, makes it possible to simulate the dissolution and transport of the various components of oil in groundwater systems. The advantages of using a modeling approach are that models can be used to anticipate the behavior of oil of any composition in any given groundwater system. The disadvantages of this approach are that the mass balance equations require the specification of parameters (such as oil solubility, sorptive capacity, and biodegradation rates), which can be difficult to determine with confidence. The limitation of using the modeling approach is to acknowledge that the model parameters needed to address the relevant questions are inherently uncertain and cannot be uniquely determined with available data. Therefore, a range of possible model parameters were used in order to illustrate, within specified bounds, the possible dissolution behavior of the residual oil and subsequent transport of PAHs in the subsurface.

Overview of the SEAM3DModel

The solute-transport code SEAM3D (Sequential Electron Acceptor Model in 3 dimensions) was designed to simulate the transport of soluble petroleum hydrocarbons, and to simulate the dissolution of non-aqueous phase liquids (NAPLs) such as oil in saturated ground-water systems (Waddill and Widdowson, 1998; Waddill and Widdowson, 2000). These reports describe the derivation of the solute-transport and NAPL dissolution equations in detail. Briefly, the solute-transport equation describes the advective transport, dispersion, sorption, and biodegradation of individual soluble petroleum hydrocarbons. The dissolution of NAPLs, which delivers soluble hydrocarbons to groundwater, is based on Raoult's Law. Raoult's Law states that the equilibrium concentration of soluble petroleum hydrocarbons in water is proportional to the solubility of each hydrocarbon and the mole fraction of each hydrocarbon in the NAPL. The rate of NAPL dissolution is specified using a mass-transfer function, and an equation of mass

balance is used to account for the change in NAPL composition over time as hydrocarbons are dissolved. SEAM3D is designed to account for a NAPL with up to 10 components with differing solubilities and molecular weights.

Description of the Model Domain

The model domain for the SEAM3D model developed in this study is based on a transect of wells installed by the Coast Guard on Grand Isle, Louisiana. The groundwater flow and solute transport domains defined by this well transect are shown in Figure 1. Groundwater flow was simulated using the U.S. Geological Survey (USGS) code MODFLOW (Harbaugh, 2005), and the domain extends 20 meters from well GIMP2 to the low-tide boundary of the beach (red box, Fig. 1). The vertical axis in Figure 1 is also in meters.
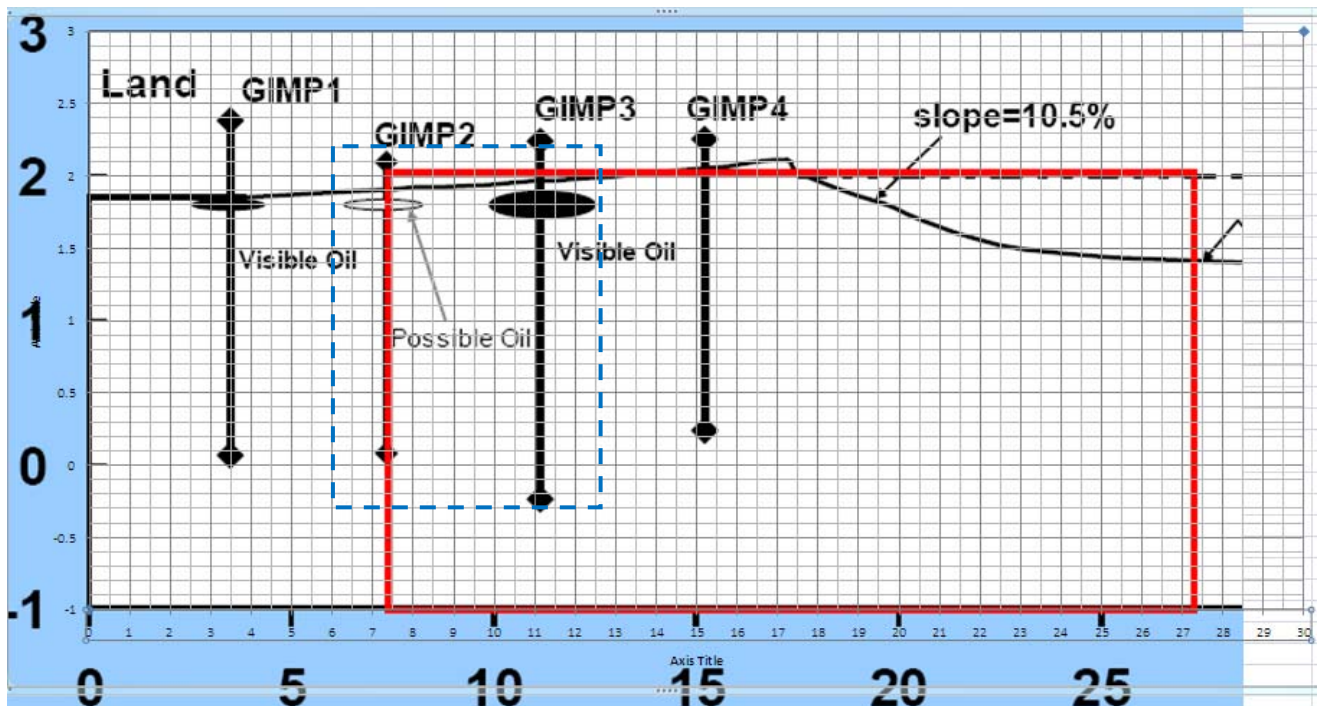

Figure 1. Cross section showing the domain of the groundwater model (red box) and the solute-transport model (dashed blue box).

The domain of the SEAM3D solute-transport model is shown in the dashed blue box in Figure 1

and is smaller than the MODFLOW domain in order to lower computational times of the simulations.

Groundwater flow underlying barrier islands is complex and affected by precipitation events and tidal cycling. No attempt was made to simulate changes in groundwater flow due to tidal changes. Rather, it was assumed that groundwater flow, on average, was from left to right, and was designed based on site measurements of hydraulic head. The boundary conditions used for the flow model (Figure 2) reflect that assumption. Uniform specified head boundaries were used on the left and right, a no-flow boundary was used at a depth of 1 meter below sea level, and a variable specified head was used to simulate the water table.
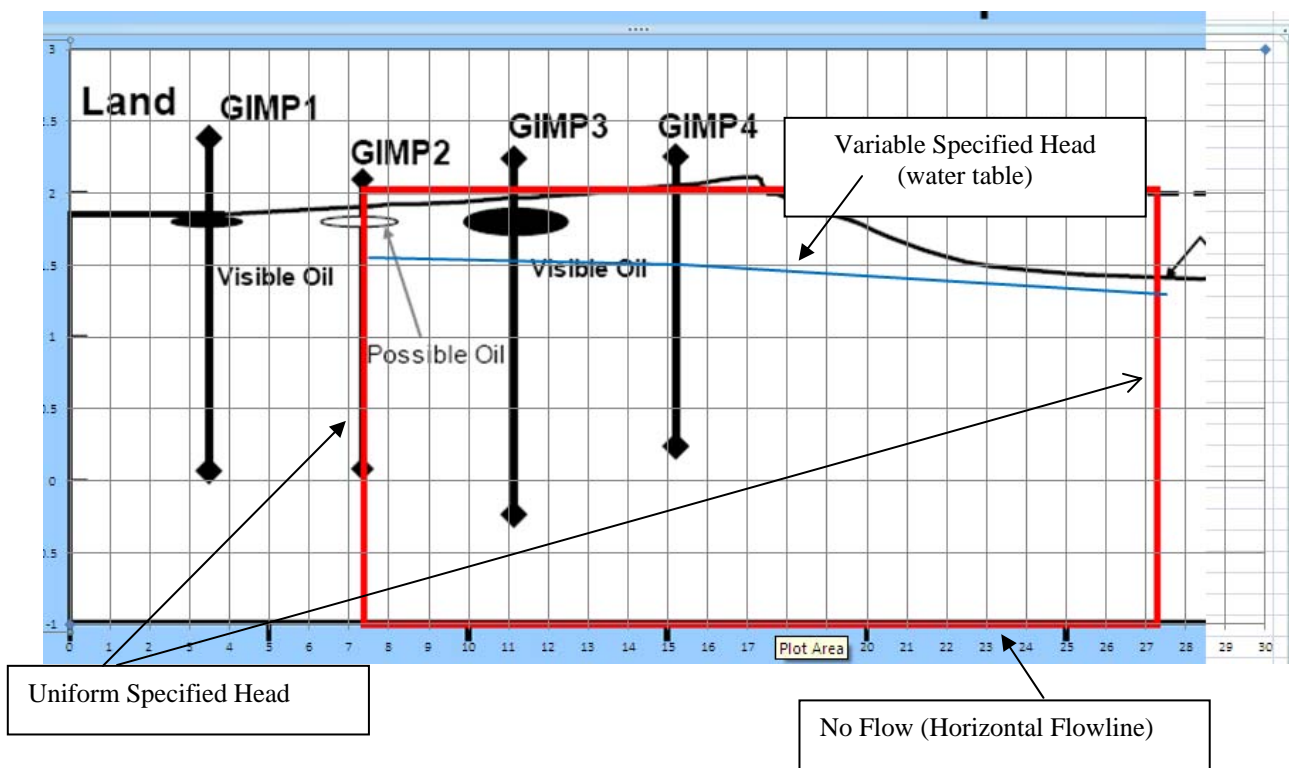

Figure. 2 Boundary conditions used for the groundwater flow model.

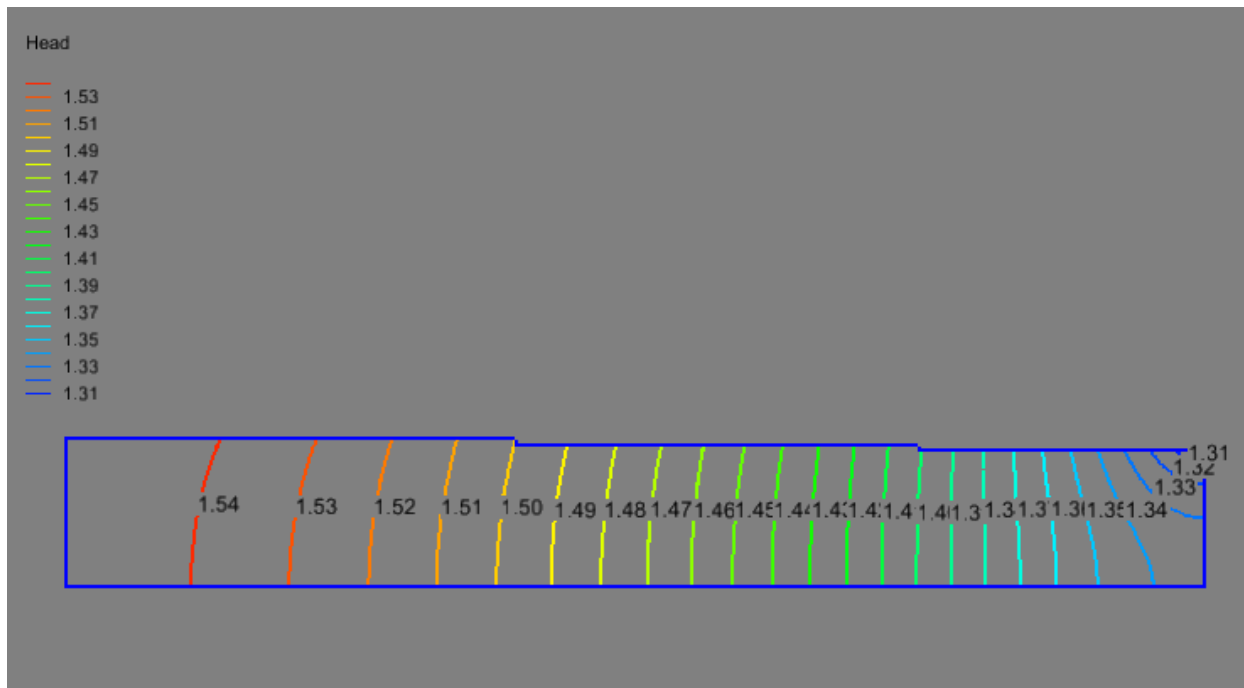The groundwater flow field generated by these boundary conditions is shown in Figure 3.

Figure 3.—Groundwater flow field generated by the model.

The groundwater flow field shows groundwater moving laterally from left to right with a total

drop in head of about 0.2 meter over the 20 meters of the model domain.

To simulate the presence of oil in the solute-transport model, it was assumed that the oil

observed at well GIMP3 was 20 centimeters thick and 2 meters long. The assumed composition

of the NAPL is shown in Table 1 and is based on analyses of weathered oil.

NAPL Constituent	Mass Fraction, m_i (g/g)	Constituent Concentration, (g/g)	Molecular Weight (g/mol)	Mole Fraction (mol/mol)	Aqueous Solubility, (mg/L)	Equilibrium Concentration (mg/L)
LPAH1	0.015	0.000105	166.2	0.02519	1.98	0.049876
LPAH2	0.01	0.00007	202.26	0.01380	0.135	0.001863
HPAH	0.025	0.000175	228.2	0.03058	0.006	0.000183
LALK	0.14	0.00098	255	0.15323	0.002	0.000306
HALK	0.66	0.00462	325	0.56680	0.001	0.000567
Aromatics	0.09	0.00063	150	0.16746	0.0005	0.000084
Inert	0.06	0.00042	390	0.04294	0	0.000000

Table 1.—Assumed composition of the NAPL used in the SEAM3D model.

The oil was assumed to consist of seven components — a light PAH with two 6-carbon rings

(LPAH1), a light PAH with 3 carbon rings (LPAH2), a heavy PAH with several carbon rings (HPAH), a light alkane (LALK), and heavy alkane (HALK), an aromatic component (Aromatics), and an inert fraction (Inert). The mass fractions assigned to each component were based on analysis of weathered oil. For the LPAH1 and LPAH2 compounds, the molecular weights, mole fractions, and aqueous solubilities were taken from the literature. For the HPAH, LALK, HALK, and Aromatic components, average molecular weights, mole fractions and aqueous solubilities were estimated from published sources. The parameters used in SEAM3D to describe flow and solute transport in are shown in Table 2.

| *Parameter*	*Base case value*	*Reference*
Horizontal hydraulic conductivity	2 m/d	Site data
Vertical hydraulic conductivity	1 m/d	*Estimate*
Effective porosity	0.30	*Estimate*
Longitudinal dispersivity	0.10 m	*Estimate*
NAPL residual saturation	0.050	Charbeneau (2007); Charbeneau and Adamski, personal communication
NAPL mass transfer coefficient	5.0 d^{-1}	Waddill and Widdowson (2000)
NAPL thickness	20 cm	Site data
NAPL width	2.5 m	Site data
Oxygen recharge concentration	1.0 mg/L	*Estimate*
Sulfate recharge concentration	500 mg/L	*Estimate*
Hydrocarbon half-saturation coefficient	0.5 mg/L	Brauner and Widdowson (2001)
Oxygen half-saturation coefficient	1.0 mg/L	Brauner and Widdowson (2001)
Sulfate half-saturation coefficient	2.0 mg/L	Waddill and Widdowson (2000)
Maximum aerobic utilization rate	0.25 mg/L per d	Brauner and Widdowson (2001)
Maximum anaerobic utilization rate	0.05 mg/L per d	Waddill and Widdowson (2000)
Oxygen use coefficient	2.0 g/g	Brauner et al (2002)
Sulfate use coefficient	4.2 g/g	Brauner et al (2002)
LPAH1 distribution coefficient (sorption)	1.4×10^{-6} m^3/g	Charbeneau (2007) *with estimate of organic carbon fraction*
LPAH2 distribution coefficient (sorption)	3.8×10^{-6} m^3/g	Charbeneau (2007) *with estimate of organic carbon fraction*
HPAH distribution coefficient (sorption)	2.0×10^{-5} m^3/g	Charbeneau (2007) *with estimate of organic carbon fraction*

Table 2.—Summary of base case input parameters for the MODFLOW and SEAM3D models.

Simulation of solute transport

The SEAM3D model was used to simulate the transport of potentially toxic LPAH1, LPAH2, and HPAH compounds from the oil body. The results of these simulations using the solubility values from Table 1 and model parameters from Table 2 are shown in Figure 4.
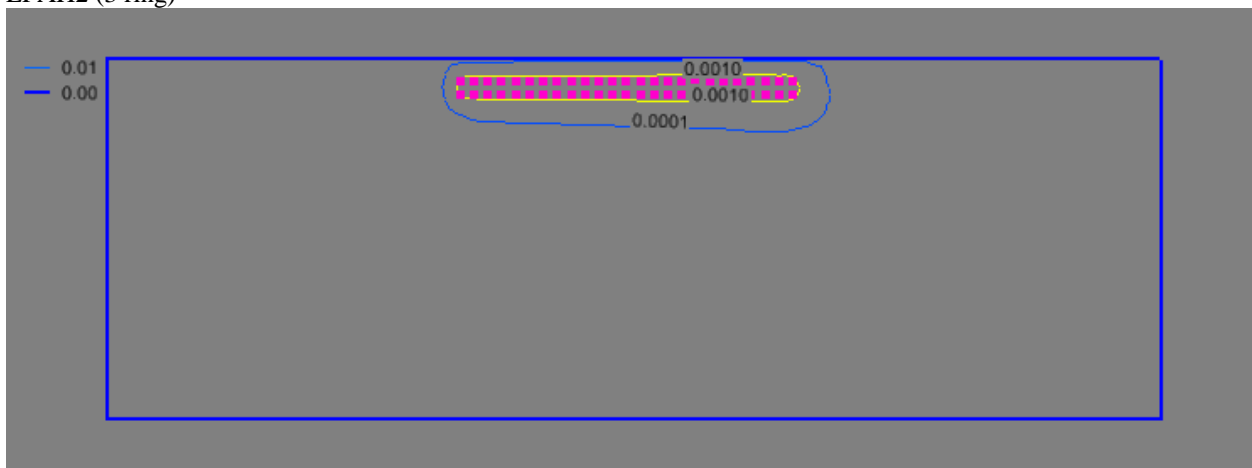
A
LPAH1 (2 ring)
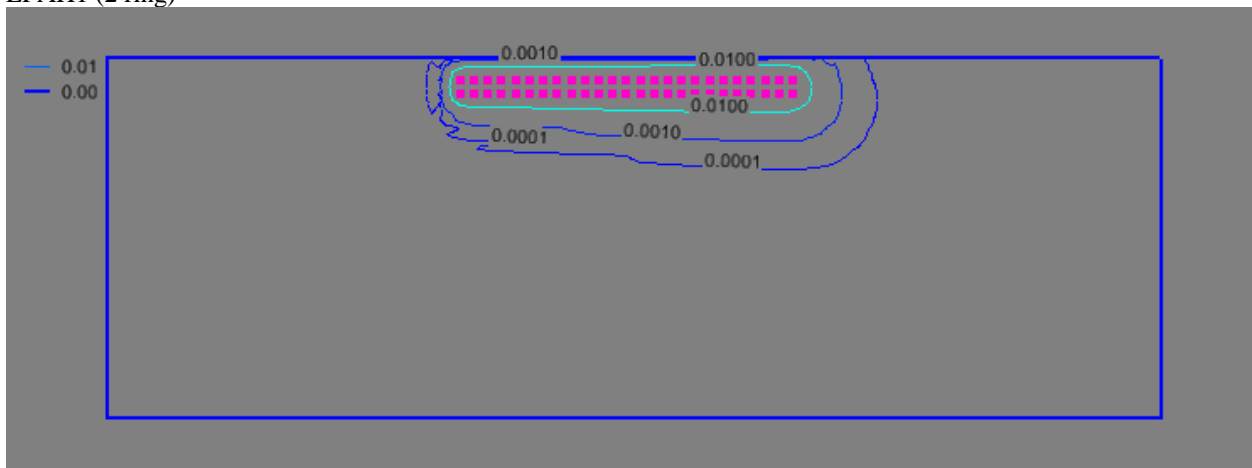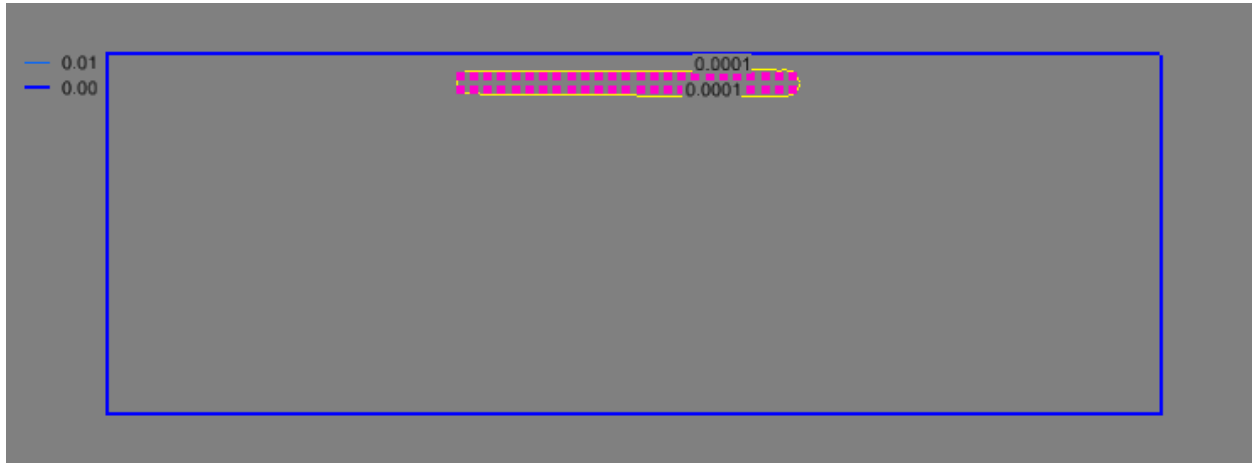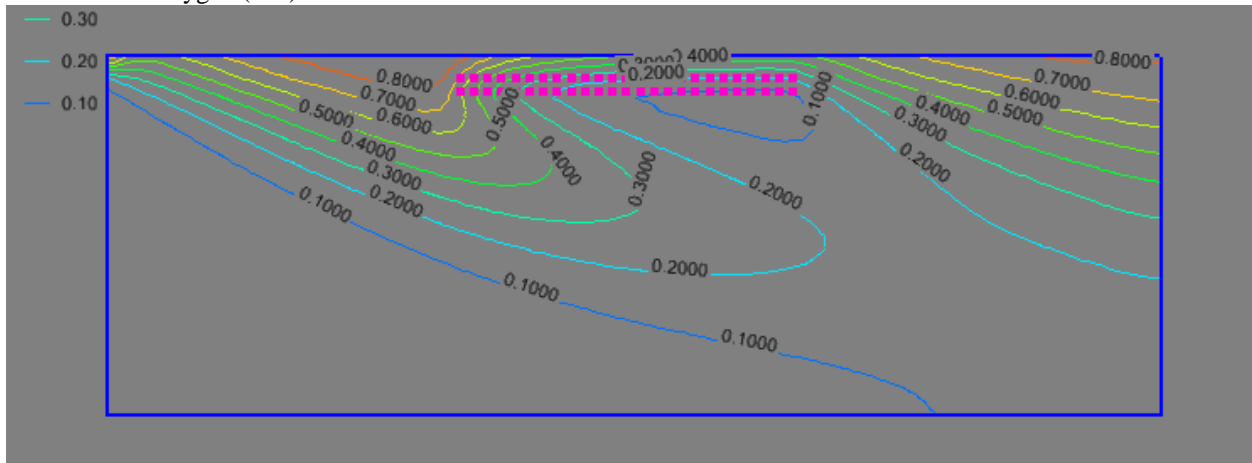

B
LPAH2 (3 ring)

C
HPAH

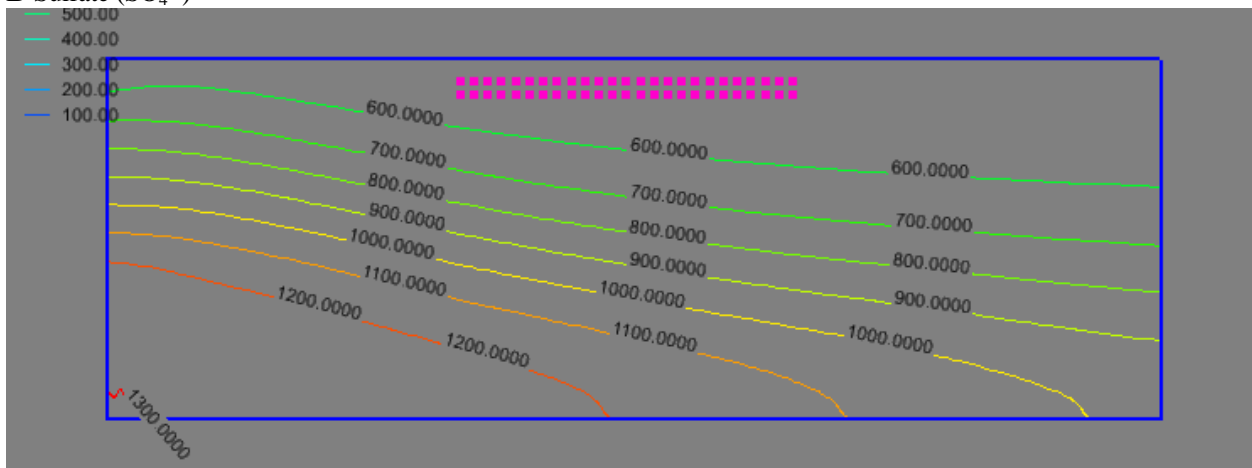Figure 4. Solute transport simulations for (A) LPAH1, (B), LPAH2, and (C) HPAH compounds.

Each of these simulations show contours of LPAH1, LPHAH2, and HPAH concentrations after less than 1 year of transport time, when compound concentration gradients had come to steady-state conditions. These simulations suggest that, assuming the well-known solubility values of LPAH1 and LPAH2 compounds (Table 1), their tendency to strongly sorb to sediments, and their biodegradability, the transport of these compounds away from the oil body will be restricted to within 1 meter of the oil body (Fig. 4A and 4B). Due to the even lower solubility and greater sorptive capacity of heavier HPAH compounds, the transport of HPAH compounds will be even more restricted (Fig. 4C).

The effects of the oil on concentrations of dissolved oxygen, sulfate, and hydrogen sulfide are shown in Figure 5. These simulations suggest that the oil will consume dissolved oxygen, creating an oxygen "sag" under the oil body (Fig. 5A). However, because of the high natural concentrations of sulfate in the groundwater, and because of the relatively low rates of biodegradation, there is no observable sag in sulfate concentrations (Fig. 5B). The effects of sulfate reduction are evident from the observed production of hydrogen sulfide under the oil body (Fig. 5C).

A Dissolved Oxygen (DO)

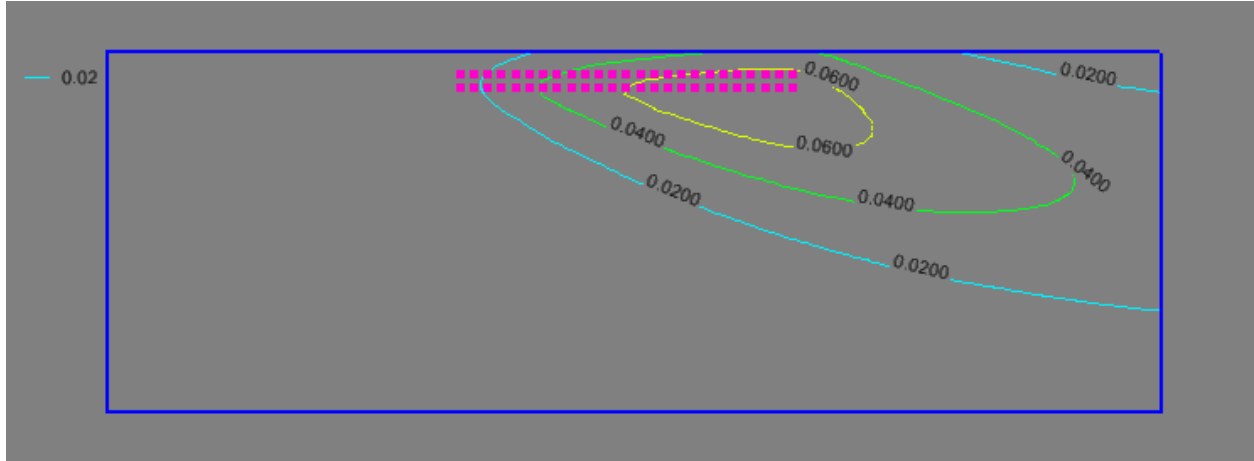B Sulfate (SO$_4^{2-}$)

C Hydrogen Sulfide (HS)

Figure 5. Solute transport simulations showing (A) the consumption of dissolved oxygen, (B), sulfate, and (C) the production of hydrogen sulfide due to oil biodegradation.

Because numerous processes such as tidal flushing and microbial growth may increase the effective solubility of the NAPL in this dynamic groundwater system, additional simulations were made assuming the solubilities were increased by a factor of 10. The results of these simulations are shown in Figure 6.

A. Solubility(x10)
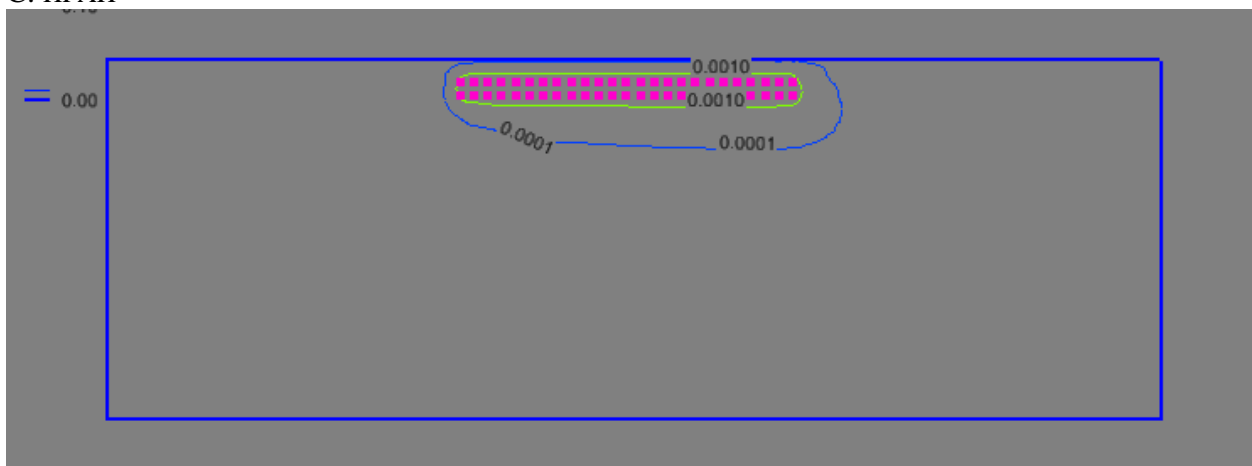LPAH1 (2 ring)
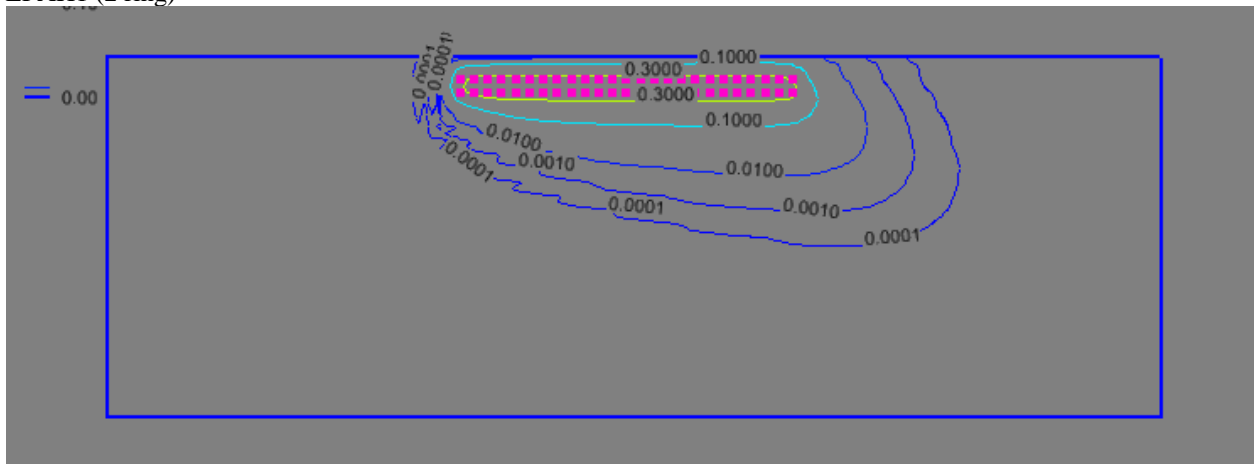
B. LPAH2 (3 ring)
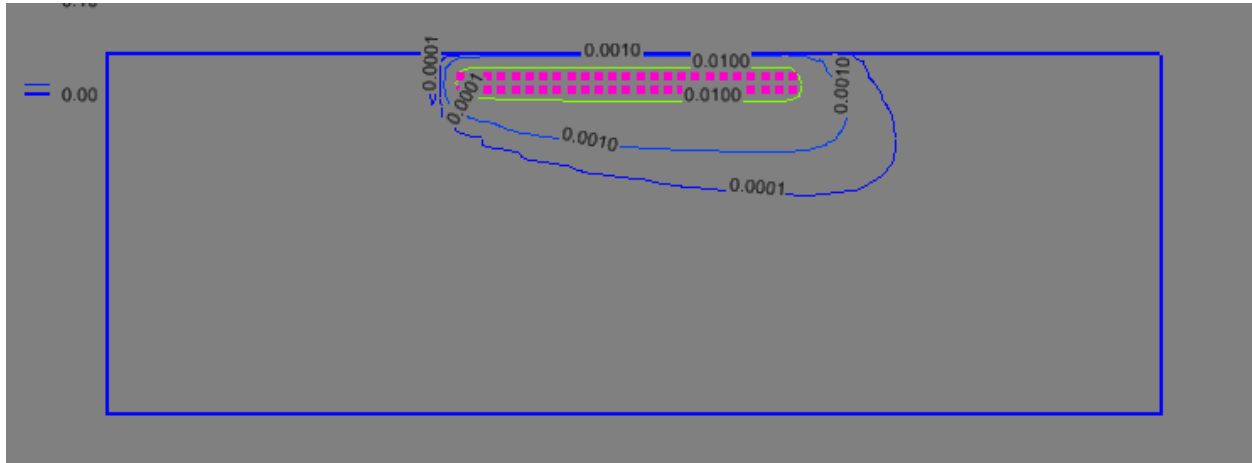
C. HPAH

Figure 6. Solute transport simulations for (A) LPAH1, (B), LPAH2, and (C) HPAH compounds assuming solubilites are 10 times the values shown in Table 1.

These simulations indicate that, even assuming relatively high solubilities of the NAPL components, solute transport of the PAH compounds will be restricted to within about 2 meters of the oil body.

Conclusions

The results of these model simulations suggest that due to the low solubility, high sorptive capacity, and biodegradability of 2-ring and 3-ring PAHs, these compounds are unlikely to be transported large distances (i.e. < 2 meters) from oil bodies by flowing groundwater. Due to their lower solubility and greater sorptive capacity, the transport of heavier PAH compounds (greater than 3 rings) will be even more restricted. This, in turn, will tend to minimize plant and

animal exposure to potentially toxic PAH compounds.

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