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Modeling of Water Quality Downgradient of a Mulch Biowall with Nearby Surface Water Receptor

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ABSTRACT: The goal of this work was to develop a model for estimating groundwater quality conditions downgradient of a biowall. Groundwater treatment biowalls may be located close to a surface water body to prevent contaminant discharges to the surface water. Groundwater contaminants passing through the biowall are treated within the biowall or immediately downgradient of the biowall. One of the effects of biowalls which use organic carbon to create anaerobic conditions as part of the designed treatment activity is the generation of anaerobic groundwater. Such groundwater conditions can lead to increased sulfide levels if influent groundwater contains moderate to high sulfate concentrations. The objective of this work was to develop a multi-component reaction model to estimate levels of sulfide present in groundwater downgradient of a biowall.

INTRODUCTION

Groundwater treatment biowalls are commonly placed at a property boundary to prevent contaminant transport off-site, or are placed adjacent to a surface water body to protect from contaminant discharges to the surface water. Groundwater contaminants passing through the biowall are treated within the biowall or immediately downgradient of the biowall. A biowall typically contains a solid organic material such as bark mulch or other agricultural waste material that serves as an electron donor to stimulate the reductive dechlorination degradation process (Henry, 2005; Parsons, 2007). One of the results of biowall treatment activity is the generation of anaerobic groundwater, which can lead to increased sulfide levels if influent groundwater contains moderate to high sulfate concentrations (Bouwer, 1994). Sulfide represents a degraded water quality of the groundwater exiting the biowall, which is of significant concern if the biowall is located in close proximity to a discharge to surface water, as shown in Figure 1. Other parameters that may represent or be related to deteriorated water quality conditions in this in situ treatment scenario include total organic carbon (TOC), nitrate, and sulfate. Common actionable levels for these parameters are listed in Table 1. The objective of this work was to create a simple chemical species model of parameters related to water quality that could then be used for predictive purposes.

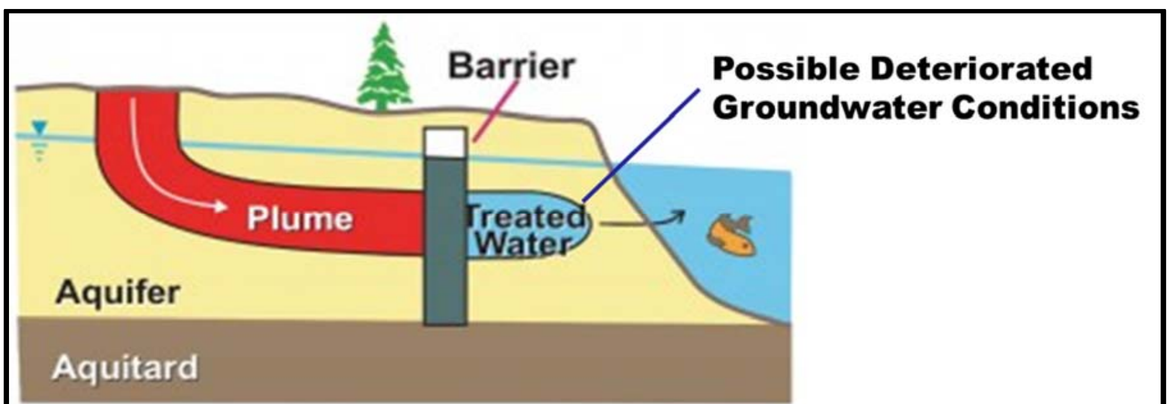

FIGURE 1. Water quality related to in situ treatment by a biowall.

TABLE 1. Applicable water quality parameter limits.

Compound	Limit	Standard Type
TOC	Generally < 10 mg/L	NPDES permits
Nitrate	10 mg/L	USEPA primary MCL
Sulfate	250 mg/L	USEPA secondary MCL
Sulfide	0.5 – 1.0 mg/L	Odor / taste

(Federal Register 1989)

MATERIALS AND METHODS

Species Modeling. A time-dependent one-dimensional fate and transport model was developed to evaluate concentrations of sulfide that may be generated in groundwater downgradient but proximate to a biowall. The model was developed by applying mass-governing equations over a control volume of the aquifer between a biowall and a nearby surface water body. The chemical species chosen for representation in the model include glucose, used as a surrogate for dissolved carbon upon degradation of solid carbonaceous material; lactate, used as a surrogate for various fatty acids appearing as a result of glucose consumption under anaerobic conditions; and finally sulfate as electron acceptor. The reaction equations involving these species are presented in equations (1) and (2) below, while the one-dimensional time-dependent mass-balance equations, which include accumulation, advection, dispersion, and reaction terms, are presented in equations (3), (4), and (5) below (Ramaswami et al., 2005).

Reaction Equations. The anaerobic biodegradation of the biomaterial is modeled with two sequential steps (glucose and lactic acid degradation):

$C_6H_{12}O_6$ (Glucose) → $2C_3H_6O_3$ (Lactic Acid) (1)

$C_3H_6O_3$ (Lactic Acid) + SO_4^{2-} → $CO_2 + H_2S + H_2O + 2H^+$ (2)

Mass Balance Equations.

Glucose: $$\frac{\partial C_g(x,t)}{\partial t} = -u\frac{\partial C_g(x,t)}{\partial x} + D_L\frac{\partial^2 C_g(x,t)}{\partial x^2} - k_1 \cdot C_g(x,t) \quad (3)$$

Lactate: $$\frac{\partial C_l(x,t)}{\partial t} = -u\frac{\partial C_l(x,t)}{\partial x} + D_L\frac{\partial^2 C_l(x,t)}{\partial x^2} + k_1 N_a C_l(x,t) - k_2 N_b C_l(x,t) C_s(x,t) \quad (4)$$

Sulfate: $$\frac{\partial C_s(x,t)}{\partial t} = -u\frac{\partial C_s(x,t)}{\partial x} + D_L\frac{\partial^2 C_s(x,t)}{\partial x^2} - k_2 N_c C_l(x,t) C_s(x,t) \quad (5)$$

The assumptions associated with this set of model equations include a homogeneous aquifer, and a uniform groundwater gradient. The model area is limited to the portion of the aquifer within only 100 feet downgradient of the biowall; therefore, these model assumptions related to aquifer uniformity are reasonable. Additionally, a first-order biodegradation rate was assumed for the glucose degradation, as well as a first order with respect to the lactate species. MATLAB was used to solve the family of differential equations using a timescale extending to approximately four years. The model constants applied to solution of the differential equations are listed in Table 2. These values were selected based upon aquifer remediation experience of the primary author. The initial and boundary conditions imposed in the solution are presented in Table 3.

TABLE 2. Model constants.

Parameters	Definition	Values
u	Groundwater velocity	0.011 ft/hr
D_L	Hydrodynamic longitudinal dispersion coefficient	0.093 ft^2/hr
L	Distance from the center of the biowall to the surface water	100ft
C_s	Initial sulfate concentration	0.3 gr/L
C_g	Initial glucose concentration	5 gr/L
k_1	Reaction rate constant for glucose degradation	1.5 hr^{-1}
k_2	Reaction rate constant for lactate degradation	0.075 L/gr-hr

TABLE 3. Initial and boundary conditions for the model.

Component	Initial Condition	Boundary Conditions	
	$t = 0$	left $x = 0$ @ $t > 0$	right x =L @ $t > 0$
Glucose(C_g)	$C_g = 0$	$C_g = 5g/L$	$\frac{\partial C_g}{\partial x} = 0$
Lactic acid(C_l)	$C_l = 0$	$C_l = 0$	$\frac{\partial C_l}{\partial x} = 0$
Sulfate (C_s)	$C_s = 0.3g/L$	$C_s = 0.3g/L$	$\frac{\partial C_s}{\partial x} = 0$

Column Experiments. Laboratory column tests were also conducted to assist in establishing a relationship among the chemical species with time. Four columns were packed with common biowall materials, specifically (a) sand only; (b) sand and mulch; (c) sand, mulch, and compost; and (d) sand, mulch, compost and emulsified vegetable oil. Deionized water was applied continuously to each column at a rate similar to the groundwater flow rate of Table 2, and samples were collected roughly once per week for TOC analysis. This column experiment was run for approximately 6 weeks. The TOC data versus time was used for comparison with the model output for TOC, which was taken as the sum of glucose and lactate parameters.

RESULTS AND DISCUSSION

The numerical solutions to the set of differential equations are presented in Figures 2, 3 and 4 below. These graphs depict the chemical species concentration profiles versus distance, with multiple curves representing different points in time. Figure 2 depicts the TOC concentration, which is the sum of the glucose and lactate concentrations from the numerical solutions. Figure 3 depicts the sulfate concentration, while Figure 4 depicts the sulfide concentration, determined as the complement of the sulfate concentration, using a constant initial baseline value of 300 milligrams/liter (mg/L) for sulfate. The first graph in each figure presents the concentration profiles in the very early stages of a newly installed biowall (1 week), while the second graph presents the concentration profiles after an extended period of time of approximately four years.

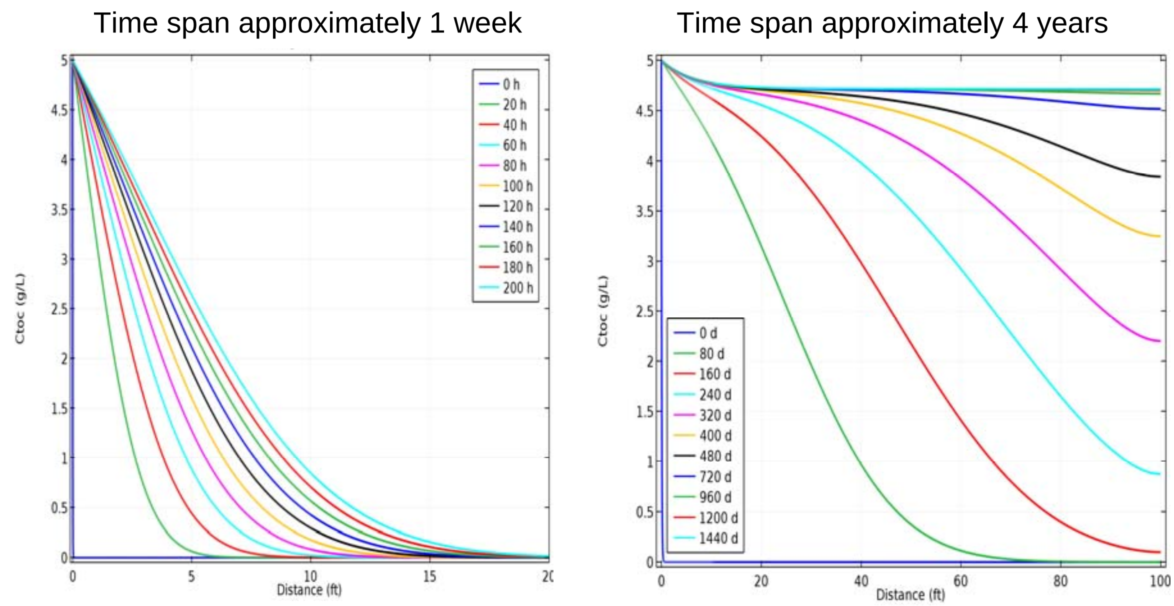

FIGURE 2. TOC modeling results as concentration versus distance profiles.

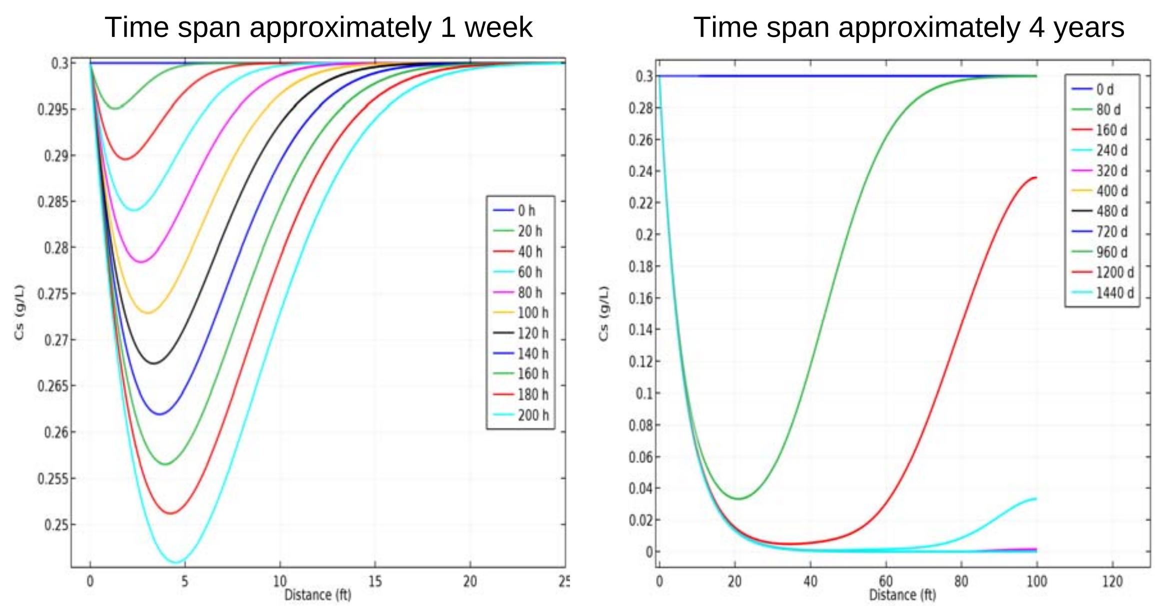

FIGURE 3. Sulfate modeling results as concentration versus distance profiles.

The TOC concentration profiles indicate TOC levels slowly increasing downgradient of the biowall until a nearly constant value of 4.7 grams/liter (g/L) is attained approximately two years after biowall installation. Figure 3 of the sulfate concentrations Indicates a low concentration envelope which expands in size with time, due to sulfate consumption as the electron acceptor in the reaction scenario. The original level of sulfate throughout the entire aquifer volume, prior to biowall installation, was 300 mg/L. The model result indicates nearly complete sulfate consumption to 20 to 40 feet downgradient of the biowall at 90 days after installation, while the entire modeled area of 100 feet downgradient is not devoid of sulfate until roughly one year after biowall

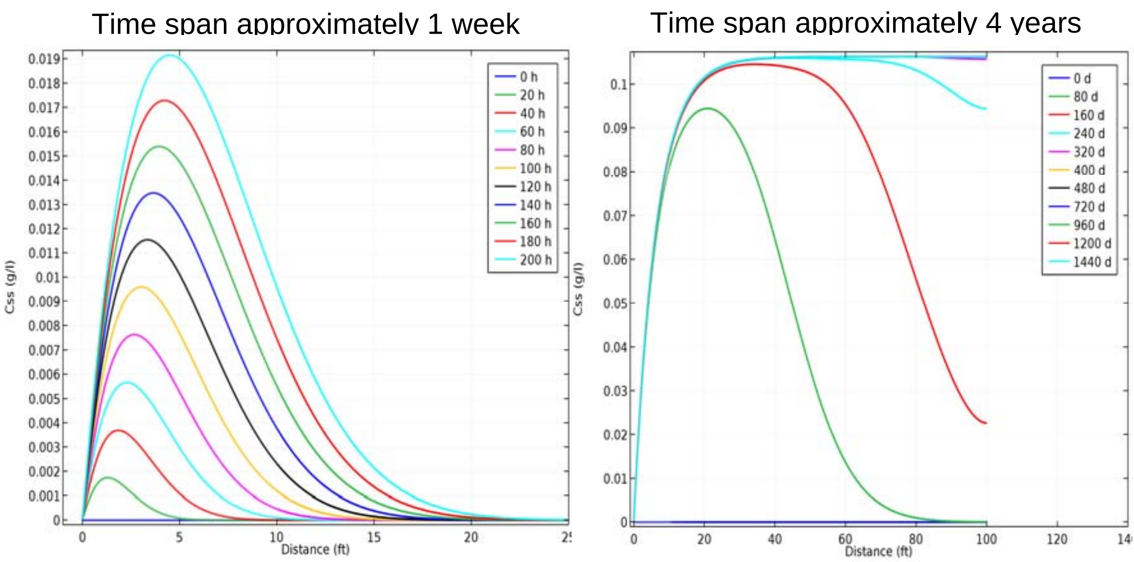

FIGURE 4. Sulfide modeling results as concentration versus distance profiles.

installation. The sulfide concentration profiles depicted in Figure 4 are a mirror image of the sulfate results, which is expected since the sulfide is the product of the sulfate reduction reaction, on a one-to-one molar basis. The second graph in Figure 4 indicates that non-zero sulfide levels may appear at the downgradient receptor (100-foot limit of the model) at a time between 80 and 160 days after the start of the biowall operation. A comparison between the laboratory column experimental results and the model results is presented in Figure 5. In this figure, the TOC concentration is depicted versus pore volumes eluted (same as time -- 1 pore volume was roughly equivalent to one week of column operation) in the experimental data or versus time in the model results. The two results show similar trends in the rise of TOC levels in the early part of the operation, however the experimental data depict a TOC decline after approximately 3 to 4 weeks, while the modeling results do not. The reason for this is that the current model does not include any exhaustion or decline in the original solid-phase carbon source, which is the likely cause of TOC decline depicted in the experimental results.

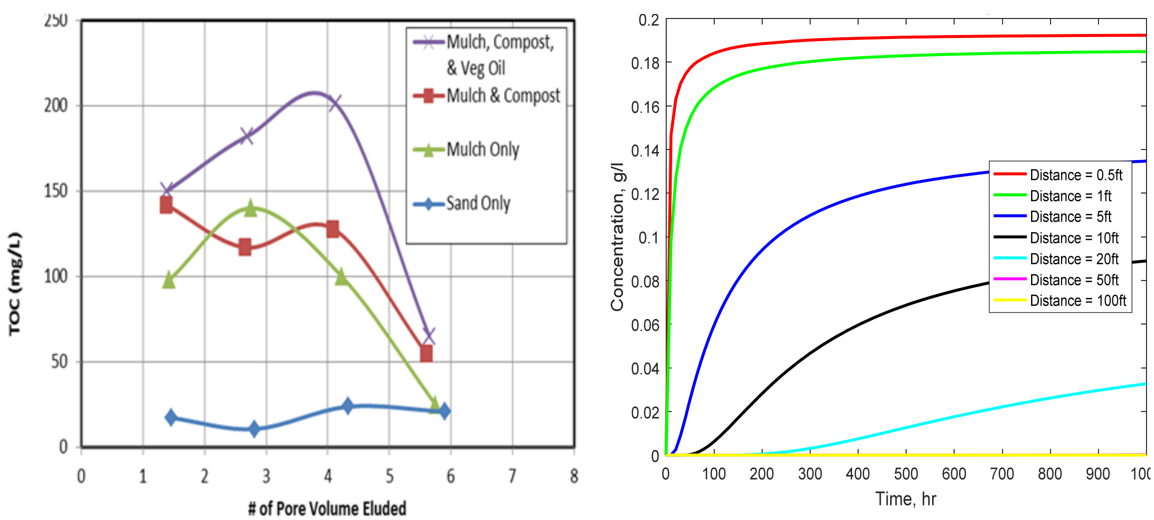

FIGURE 5. Column test results for TOC, alongside TOC modeling results.

CONCLUSIONS

The model results provide insight into the advance of sulfate, sulfide, and organic carbon levels in groundwater downgradient of a biowall, and in close proximity to a surface water receptor. The carbon source, sulfate and sulfide data are compared to laboratory column data. The end result in the model simulation data indicates that high sulfide concentrations can occur hundreds of feet downgradient of a biowall within roughly one year of the biowall installation. Thus, the concentration profiles can be used as a predictive tool for biowall operation. The results suggest future work should concentrate on adjustment of the model parameters and equations to more accurately represent laboratory column data for TOC in which exhaustion of the carbon source occurs after an initial period of time of biowall operation.

ACKNOWLEDGMENTS

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