Soil biofilm attachment/detachment effects =  $-(V)(R_{nd})(SSA)(X)$ 

Combining the terms, setting  $V = A\Delta x$ , and simplifying,

$$\frac{\partial X}{\partial t} = -\{(Q/A + (E_f)(k_e)))[\frac{\partial X}{\partial x}]\} + \{(D\frac{\partial^2 X}{\partial x^2}\} - (R_{nd})(SSA)(X) - (k_d)(X) - \frac{\partial X}{\partial t}] = -[U + (E_f)(k_e)]\frac{\partial X}{\partial x} + D\frac{\partial^2 X}{\partial x^2} - [(R_{nd})(SSA) + k_d](X)$$
(1)

At steady state:

$$0 = -[U + (E_f)(k_e)]\frac{\partial X}{\partial x} + D\frac{\partial^2 X}{\partial x^2} - [(R_{nd})(SSA) + k_d](X)$$

The above model yields a form that is similar to the advective-dispersive transport model for aqueous contaminants, except that it accounts for electrophoresis and soil biofilm effects. Inhibition effects can easily be incorporated into the model developed in this paper by modifying the decay rate expression with a Monod kinetics model and the appropriate type of inhibition model – noncompetitive, competitive or uncompetitive inhibition model.

In the above model, it is apparent that the electrophoretic transport and advective transport terms are both dependent on the concentration gradient. The biofilm attachment and the net decay term are a function of the bacterial concentration in the pore fluid. In fine-grained soils the groundwater velocity is likely to be very low. In fact this is the driver for applying an electric field so that microorganism transport can be achieved under an applied electric field rather than under the hydraulic gradient alone.

Bacterial transport rates have been reported to be around  $4 \text{ cm}^2/\text{V/h}$  (Deflaunn and Condee, 1997; Wick et al., 2004). Past studies in our laboratory have shown that aerobic microorganisms can be transported successfully at field strengths as low as under 0.5 V/cm (Maillacheruvu and Chinchoud, 2011). More importantly, the transported microbes were capable of retaining their activity (capacity to break down the organic) after being transported through porous media under the influence of electric fields.

We can develop condition numbers to analyze the effects for a different range of values for the parameters under consideration. For this analysis, the impact of diffusion is not included but all other effects are included. The product " $(E_f)(k_e)$ " can be expressed as K and the product " $(R_{nd})(SSA)$ " can be expressed as R. The concentration of bacteria in the pore fluid at steady state can be expressed as:

$$\mathbf{X} = \frac{U+K}{U+K+R+k_d} \mathbf{X}_0$$

where  $X_0$  is the initial concentration of bacteria in the pore fluid

The condition numbers for "Q" can be written as:

$$CN_{U} = \frac{U}{X} \frac{\partial X}{\partial U} = \left[\frac{1}{U+K} - \frac{1}{(U+K+R+k_{d})}\right]U$$

The condition number of "K" can be written as:

$$CN_{K} = \frac{K}{X} \frac{\partial X}{\partial K} = \left[ \frac{1}{U+K} - \frac{1}{(U+K+R+k_{d})} \right] K$$

Condition numbers were derived similarly for other parameters.

### **RESULTS AND DISCUSSION**

Using the developed expressions for the condition numbers and assuming the following average values as shown below, the relative impact of the electrophoresis and advection on bacterial transport in the pore fluid can be estimated. As an example, if the average values of the parameters are:  $R = 0.001 \text{ day}^{-1}$ ;  $k_d = 0.1 \text{ day}^{-1}$ ; K = 0.5 m/day; U = 0.002 m/day, the condition numbers can be calculated to be:

 $CN_U = -1.997$  $CN_K = -499.3$ 

Clearly the impact of the electrophoretic mobility is much higher in a fine grained soil. Another way to evaluate the impact is as follows. If an electric field strength of 0.5 V/cm is applied for a bacterial transport rate of 4  $\text{cm}^2/\text{V/h}$ , how does that compare to the impact of advective transport for a porous medium with a hydraulic conductivity of 1 x  $10^{-6}$  m/s, porosity of 0.40, and a hydraulic gradient of 0.01? The calculation shows that electrophoretic transport should be around 2 cm/h and the seepage velocity is just under 3 orders of magnitude lower. The same equations can be used to estimate the impact in a coarse grained soil where the seepage velocity is significantly higher. If the seepage velocity were 2 magnitudes higher (U = 0.2 m/d), the impact of electrophoresis and seepage velocity is comparable ( $CN_{II} = -199.7$ ;  $CN_K = -499.3$ ). If the seepage velocity were 4 magnitudes higher (20 m/d), electrophoresis effects would be negligible compared to hydraulic transport phenomena ( $CN_{IJ} = -19970$ ;  $CN_K = -499.3$ ). The relative impact of the different parameters on the advective-dispersive-reaction model was evaluated using a Monte Carlo-based analysis on the condition numbers (CNU, CNK, CNR, and CNkd) for the different parameters (U, K, R, kd). Results based on a 1000-run simulation showed that the impact of K (electrophoretic transport parameter) and  $k_d$  (decay rate parameter) were about the same order of magnitude. Table 2 presents the summary from these analyses for condition numbers for the four different parameters analyzed in this study. The range for the four parameters selected in the analyses is shown below and the average of the 1000 Monte Carlo simulations is also shown. Table 2 also shows the range and average values for the parameters in

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this study. The average values in Table 2 were calculated from the Monte Carlo simulations.

Parameter	Minimum	Maximum	Average
U	0.0002	0.0200	0.0101
k	0.0500	1.0000	0.5250
R	0.0001	0.0100	0.0051
k <sub>d</sub>	0.0100	1.0000	0.5050

 Table 2. Summary of Results from Monte-Carlo Based Analyses

Table 3 provides a summary of the standard deviation, as well as maximum and minimum values for the condition numbers obtained from the Monte Carlo analysis.

Table 5. Summary	of Results II	rom Monte-Car	lo Based Analyses

	CNU	CN <sub>K</sub>	CN <sub>R</sub>	CN <sub>kd</sub>
Average	0.0178	0.4691	0.0059	0.4811
Standard deviation.	0.2189	0.9042	0.0694	0.9169
Maximum	0.2190	0.9181	0.0694	0.9275
Minimum	0.0001	0.0139	0.0001	0.0106

Table 4 shows the summary of the relative values of the condition numbers for the four parameters analyzed in this study. These data show that the relative contribution of the condition number for parameter "U" and "R" are low, indicating that they do not impact the microbial transport substantially. In contrast, the other two parameters "K" and "k<sub>d</sub>" have relative contributions of 49% and 48%, respectively.

Results presented in Table 4 indicate that the impact of both K and  $k_d$  was at least one order of magnitude higher than the impact of U (advective transport parameter) or R (parameter relating to microbial attachment to soils) for fine-grained soils.

<b>CONDITION NUMBER</b>	<b>RELATIVE CONTRIBUTION</b>
CNU	2%
CN <sub>K</sub>	49%
CN <sub>R</sub>	1%
CN <sub>kd</sub>	48%

## **Table 4. Relative Impact of Parameters**

Figure 1 shows the variation of  $CN_K$  with parameter K. Figure 2 shows the variation of  $CN_{kd}$  with parameter  $k_d$ . Relationships between the condition numbers for each parameter and the values of the four parameters were also analyzed but are not included in this paper. Figures 1 and 2 indicate that the condition numbers for the

electrokinetic transport parameter "K" and the decay rate coefficient " $k_d$ " are both clustered around 0.50. These results suggest that for fine-grained soils, the other parameters considered in this paper, namely bacterial adhesion to soils and the advective transport, are not likely to impact electrokinetic transport of microorganisms in the subsurface.



## FIG. 1. Condition number analysis for electrokinetic transport parameter "K".

These results are consistent with expected results for coarse-grained versus finegrained soils. For coarse-grained soils, one would expect that advective transport would be significant, since hydraulic conductivity is typically a few orders of magnitude higher than for fine-grained soils. It also follows that the measurement of electrophoretic parameters for a fine-grained soil is critical in evaluating microbial transport and the hydraulic transport mechanism is essentially negligible for finegrained soils. Consequently, the transport equation can be modified for the appropriate soil conditions, so that the solution is computationally easier. In many cases, it might be acceptable to drop the diffusive transport term if electrophoretic processes are in effect. Results shown in Table 4 and Figure 2 suggest that the impact of microorganism decay in the subsurface environment is critical. For effective electrokinetics-enhanced bioremediation, it is important to transport the microorganisms as well as have them retain their activity to be able to break down or transform the contaminant of interest. It therefore appears that both these parameters are critical in modeling electrokinetic transport of microorganisms under low-strength electric fields.

Under certain boundary conditions and soil fabric and pore-fluid might warrant inclusion of additional terms in the model. In these cases, one can include hydraulic and electrophoretic transport, as well as diffusion in the different directions to develop a more complex 3-dimensional model.



FIG. 2. Condition number analysis for microorganism decay.

The potential for electrokinetics-enhanced remediation under anaerobic conditions is vastly untapped. The generation of oxygen from applying low-strength electric fields might present a problem for anaerobes. The site of oxygen generation should therefore be different than the location of anaerobes, for the treatment to be effective. However, it is well known that oxygen production occurs in the electrode wells and the diffusion of oxygen through the soil matrix is limited, which is promising for EK-driven anaerobic bioremediation technologies. For an oxygen diffusion coefficient value of about 2.0 x  $10^{-5}$  m<sup>2</sup>/s it can be shown that the depth of penetration of oxygen is less than 300 mm, even if the soil is exposed to air directly. Therefore, the distance of penetration of oxygen under several feet of soil may be reasonably expected to be much smaller. Aerobic microenvironments or pockets of oxygen might persist but their impact on the overall anaerobic bioremediation is likely to be minimal. Studies in our laboratory over the years also show that anaerobes are indeed able to survive and function in the presence of small quantities of oxygen.

The more important question is whether these microorganisms are able to retain their potential (activity) to break down toxic organics such as PAHs, chlorinated organics and other hazardous wastes? Studies in our laboratory have shown that anaerobic enrichment cultures developed from local anaerobic digesters were successful in breaking down different polyaromatic hydrocarbons (PAHs) such as naphthalene, phenanthrene, and pyrene (Maillacheruvu and Pathan, 2009). Wu et al. (2012) and Mao et al. (2012), and Gent et al. (2014) have reported on successful bioremediation of chlorinated solvents using EK-bio methods.

These studies with PAHs and chlorinated solvents demonstrate the potential for anaerobic microorganisms to clean up contaminated soils *in situ* as an attractive alternative to more expensive remediation options such as excavation and *ex situ* treatment. The model developed in this paper can be adapted for modeling the transport of anaerobic microorganisms and solutes under electric fields in the subsurface environment.

# CONCLUSIONS

A one-dimensional model to describe the transport of microorganisms under electric fields was presented in this paper. Many existing models focus on describing the fate and transport of aqueous phase contaminants in the subsurface. The relatively simple one-dimensional model was developed in this study with a hypothesis that excluding some parameters and excluding some processes can actually simplify the solution without sacrificing accuracy. In general the more complete model will include a variety of processes and therefore terms. There is certainly a limit to excluding processes and parameters because at some stage the model will not resemble the actual processes in the subsurface. However there is uncertainty associated with each introduced parameter. It is likely that excluding parameters and some processes that have minimal impact on the solution will improve the accuracy of the model prediction because the scatter is also likely to be lower with fewer parameters. Uncertainty analyses, using Monte Carlo simulation showed that for fine-grained soils, parameters relating to electrophoretic mobility and bacterial decay rate impacted the microbial transport the most.

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## Optical Detection of Volatile Hydrocarbons during the Electrokinetic Treatment of Polluted Soil Using an Optical Fiber Modified with a Composite of Prussian Blue and an Acrylic Polymeric Emulsion

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Abstract: Exposure to volatile hydrocarbons may lead to increased health risks. Consequently, there is an important interest in sensor development to detect and monitor the presence of these compounds, particularly at low concentrations. There are different kinds of detectors of volatile hydrocarbons (VHC), such as optical sensors, which have been developed by employing the phenomenon of evanescent fields for the detection of volatile organic compounds (VOC) such as hydrocarbons which include unclad, tapered and bendable fibers. However, the preparation of these fibers requires structural modification of the coating and therefore the sensor becomes fragile. These devices can only be used where there are no mechanical processes that may damage them. In this research, the optical detection of VHCs generated by electrokinetic treatment of polluted soil was evaluated. This evaluation was done by developing a fiber optic cable that was reduced in diameter to 20  $\mu$ m and modified with a composite of Prussian blue and an acrylic polymeric emulsion to monitor the removal of hydrocarbons from soil when applying an electrical field.

## **INTRODUCTION**

VOCs are commonly used as ingredients in household products, industrial processes in various areas such as agriculture, environment, biology, medicine, defense, transportation, industry, safety at work, refineries, among others, where they typically vaporize at ambient conditions and can be inhaled, leading to health damage (Elosua et al., 2006). However, for gas monitoring, it is necessary to employ equipment such as gas chromatography and sampling systems to collect samples in the field as well as special filters, which are reflected in the time and cost of analysis.

In recent years, research on the development of VOC sensors has increased with the motivation for many applications, such as in the food industry, chemical industry, electronic noses and others (Lee, 2003). Sensors for the detection of gases have been developed, which are electrochemical sensors and semiconductor-based sensors (pellistors), but these have limitations in terms of life span, susceptibility to short circuit, cost, among others. In contrast, optical gas sensors offer fast response times (real time in some cases), high specificity, do not need reference systems, there is no consumption of the analyte, are subject to miniaturization, can be monitored remotely

and can create sensing networks (Calle et al., 2000; Francis et al., 2002; Moh, et al., 2012).

One of the most-used configurations in the manufacture of optical sensors is that in which optical fiber is employed, which is modified physically and chemically to detect a particular analyte. To confine the optical wave in the core using optical fiber, it is necessary to use several structural modifications in order to have interaction with the environment. Among some of the fiber optic devices developed for this purpose, there are tapered fibers, uncoated fibers (UF), heterocore fibers (HF), polished fibers, Bragg gratings (BOF), long period gratings (LPF), among others (Augousti et al., 1999; Wolfbeis et al., 2004; McDonagh et al., 2008).

However, in some devices, the coating removal becomes a complicated process and the optical fiber becomes brittle and prone to fracture. In the case of BOF and LPF, there are more complicated monitoring spectral shifts due mainly to the high cost of equipment, in addition to being very sensitive to temperature changes, and it is necessary to make appropriate compensations.

An alternative to avoid these difficulties is the use of heterocore fiber devices. These devices are fabricated by joining fibers with different core sizes, in particular by inserting a small section (in mm) of single mode fiber (SMF) between sections of multimode fiber (MMF) as shown in FIG. 1. This causes the optical wave traveling through the core of the MMF fiber to expand in the cladding of the SMF, being guided by the waveguide formed by the SMF cladding and air, so it can easily interact with the external environment (Luna et al., 2007; Seki et al., 2007; Monzon et al., 2009; Seki et al., 2009; Akita et al., 2010).



FIG. 1. Diagram of a heterocore optical fiber.

In this sense, the optical fiber device developed for the detection of VOCs has been used for the detection and quantification of some VOCs such as, acetone, chloroform, dichloromethane, methanol, among others. The results were used to construct the graph in FIG. 2, where the compounds with a refractive index lower than 1.4 showed signals with a positive slope as with acetone (n = 1.359), while compounds with a refractive index higher than 1.4 showed a negative slope as with dichloromethane (n = 1.424) and chloroform (n = 1443). This principle of operation of the optical fiber allows a qualitative VOC analysis. Consequently, in this research the goal is the optical detection of volatile hydrocarbons during electrokinetic treatment of polluted



FIG. 2. Detection of different VOCs and the relationship to their refraction indexes for acetone, dichloromethane and chloroform.

## **EXPERIMENTAL DEVELOPMENT**

### Modified fiber optic with APE/PB.

For the preparation of the composite of acrylic polymer emulsion/Prussian blue (APE/PB), 50% APE (Acrilex, 100%) and 4mM PB in a 50:50 ratio were used. PB was synthetized from potassium ferrocyanide (JT Baker, 99.5%), ferrous chloride (JT Baker, 100%) and potassium chloride (Golden Bell, 99.6). The heterocore device fabrication was accomplished by splicing a 1 cm single-mode fiber (5/125 microns) between two sections of multimode fiber (62.5/125 microns). Subsequently, the fiber was coated by dip coating in a container with a capacity of 50  $\mu$ L for 5 minutes of immersion and then dried at room temperature for two hours.

### Electrokinetic treatment monitoring process using APE/AP/FO.

One of the options for a field application of a fiber optic device is monitoring the electrokinetic treatment. This process is carried out by monitoring the process in the laboratory. In order to monitor the electrokinetic treatment, tests were carried out using two cell configurations, a 1D system and 2D circular arrangement system (Corona *et al.*, 2010, A). Both configurations were carried out under the same conditions of temperature (25 °C) and as closed systems. The parameters used for the electrokinetic treatment were, for both systems, a potential of 30 volts using 0.1M NaOH as the supporting electrolyte and as electrodes, a Ti cathode and an IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>