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Design of aquifer remediation systems: (2) Estimating site-specific performance and benefits of partial source removal[☆]

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Abstract

A Lagrangian stochastic model is proposed as a tool that can be utilized in forecasting remedial performance and estimating the benefits (in terms of flux and mass reduction) derived from a source zone remedial effort. The stochastic functional relationships that describe the hydraulic “structure” and non-aqueous phase liquid (NAPL) “architecture” have been described in a companion paper

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(Enfield, C.G., Wood, A.L., Espinoza, F.P., Brooks, M.C., Annable, M., Rao, P.S.C., this issue. Design of aquifer remediation systems: (1) describing hydraulic structure and NAPL architecture using tracers. *J. Contam. Hydrol.*). The previously defined functions were used along with the properties of the remedial fluids to describe remedial performance. There are two objectives for this paper. First, is to show that a simple analytic element model can be used to give a reasonable estimate of system performance. This is accomplished by comparing forecast performance to observed performance. The second objective is to display the model output in terms of change in mass flux and mass removal as a function of pore volumes of remedial fluid injected. The modelling results suggest that short term benefits are obtained and related to mass reduction at the sites where the model was tested.

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1. Introduction

The number of hazardous waste sites across the United States has grown to approximately 217,000, with billions of cubic meters of soil, sediment, and groundwater plumes requiring remediation (NRC, 2003). Pump-and-treat has been (Kovalick and Fiedler, 1998) and continues to be the remedial technology of choice for the majority of contaminated groundwater aquifers. At the present time, it appears to be technically impracticable to remove all of the contamination from sites contaminated with non-aqueous phase liquids (NAPLs) with currently available remediation technologies. Without being able to show an immediate benefit beyond accelerated mass depletion from using an aggressive technology, there is little incentive for decision makers to implement more expensive alternatives (NRC, 1997). Pump-and-treat systems for dissolved contaminants are being optimized to minimize cost (Mayer et al., 2002). This is a computationally expensive task for groundwater flow problems. Commonly used numerical models capable of accurately describing multiphase fluid and contaminant flow require significantly more input data and are more computationally expensive than the simpler water transport models. Optimization with these existing codes may not be feasible. To compete with an optimized pump-and-treat technology, aggressive remedial technologies will need models that incorporate the operational and environmental complexity and can be used to minimize the cost of the technology and show short term environmental benefit in terms of reduction in the average flux leaving the source zone. This contribution provides a simplified analytic model addressing the complex problem that is suitable for optimization in many field situations.

There are five primary pieces of information required before one can estimate the performance of an extraction based remedial technology. One needs to be able to describe: (1) the movement of a fluid through the flow field; (2) how the NAPL is distributed throughout the flow field; (3) the solubility of the contaminant of interest in each of the remedial mixture(s); (4) how the remedial mixtures are injected into the flow field (volume, duration, and sequence); and (5) the mole fraction of the contaminant of interest in the NAPL. Previously, Enfield et al., (this issue) presented an approach to describe the hydraulic structure which controls the movement of water through the flow

field and how the NAPL is distributed throughout the flow field in terms of a NAPL architecture. The objective of this paper is to use this information in a simple computational frame work and estimate contaminant elution curves resulting from in situ flushing of a contaminated formation and evaluate the near field benefits (change in mass or change in average mass flux) of the flushing.

2. Methodology

Streamline modelling approximates 3-D fluid flow by a sum of 1-D solutions along streamlines. Details of streamline simulations can be found elsewhere (Crane and Blunt, 1999). A key to streamline simulation is decoupling water flow from chemical transport. Thus, the approach is valid only under conditions where the NAPL phase is stationary. This is a reasonable assumption at most field sites when remediation is being considered and tracer studies are being performed. The hydraulic “structure” as presented in a companion paper (Enfield et al., this issue) is described by two parameters (a geometric mean and standard deviation) that characterize a population of “travel times” for individual 1-D streamlines. These “travel times” are functionally coupled to NAPL saturation by way of the NAPL “architecture”. Simple problems like the movement of tracers that do not dissolve the NAPL can be solved analytically using temporal superposition of finite pulses. To apply the approach to the current objective, that is to remove NAPL, additional simplifying assumptions that the NAPL removal does not impact the flow field were made. The flowfield was divided into what will be called flowtubes using the probability inverse function with each of the j flowtubes having equal water flux. As discussed in Enfield et al. (this issue) a population of flowtubes has specified statistical properties that describe the hydraulic structure and NAPL architecture. These flowtubes could also be viewed as analytic elements since the flow within each flow tube is solved analytically. Further it was assumed that the remedial fluid and NAPL in a given flow tube are in chemical equilibrium. For solubilization-based remedial approaches, for a specific flow tube (j), calculation of the number of pore volumes (PV_{cj}) of a specific remedial fluid (r) required to dissolve a neat NAPL is based on the mass of NAPL and the solubility of the contaminant (i) in the remedial fluid (\hat{S}_{ir}) (mol/L) as follows:

$$PV_{cj} = \frac{S_{nj}\rho_n}{(1 - S_{nj})\hat{S}_{ir}MW_n} \quad (1)$$

where (S_{nj}) is the NAPL saturation, (ρ_n) is the NAPL density (g/L), and MW_n is the average molecular weight of the NAPL (g/mol).

At most field sites the contamination is a mixture of contaminants rather than a neat NAPL. Raoult’s Law has been applied to mixtures to relate solution concentration and solubility (Banerjee, 1984). In Raoult’s Law nomenclature

$$C_i = \chi_i \gamma_i \hat{S}_{ir} \quad (2)$$

where χ_i and γ_i = mole fraction and the activity coefficient of the solute i , respectively; and \hat{S}_{ir} = the solubility of component i in the remedial fluid r . In situations where the NAPL

constituents have similar properties the activity coefficient is approximately 1 (Cline et al., 1991). Assuming the activity coefficient is one, Eq. (1) can be rewritten as

$$PV_{cj} = \frac{\chi_i S_{nj} \rho_n}{(1 - \chi_i S_{nj}) \chi_i \hat{S}_{ir} MW_n} \quad (3)$$

If one solves the flow problem as a moving boundary problem, with instantaneous reactions at the boundary, considering only an initial fluid (to establish initial conditions) and a single remedial fluid, it is easy to estimate the concentration eluting from a given flow tube (C_{ej}) based on which fluid is eluting, the solubility of the contaminant in the eluting fluid (\hat{S}_{ir}), and whether there is any NAPL in the flow tube of interest.

$$C_{ej} = C_{ij} \quad \text{for } J_j < 1 \quad (4)$$

$$C_{ej} = \chi_i \hat{S}_{ir} \quad \text{for } 1 \leq J_j \leq PV_{cj} + 1 \quad (5)$$

$$C_{ej} = 0 \quad \text{for } J_j > PV_{cj} + 1 \quad (6)$$

where J_j is the number of pore volumes of remedial fluid eluted and C_{ij} is the initial concentration in the j th flow tube.

$$C_{ij} = 0 \quad \text{for } S_{nj} = 0 \quad (7)$$

$$C_{ij} = \chi_i \hat{S}_{iw} \quad \text{for } S_{nj} > 0 \quad (8)$$

where \hat{S}_{iw} is the contaminant solubility in water (assumed to be the resident fluid at the initiation of remediation). By calculating the temporal response of C_{ej} for each of the flowtubes and combining the results using spatial superposition, one obtains the flux-averaged concentration at the sampled time. Theoretically, this is true only for the most soluble compound in the NAPL. Dissolution progresses from the upgradient end of the NAPL body. Under equilibrium conditions with no dispersion or diffusion the most soluble compound is depleted before the second-most soluble compound is depleted. After each compound is removed, the mole fractions change. The dissolution of each successive solubilized compound is based on the revised NAPL saturation and composition. Revised variables (χ_i and S_{nj}) are dependent on the initial NAPL saturation and composition, as well as the mole fractions of the compounds more soluble than component i . It is assumed that the remedial fluid do not change the sequence of solubilization.

As implemented here the remedial program consists of an initial fluid used strictly for calculating C_i . This “computational fluid” does not remove any NAPL. The initial fluid is followed by a sequence of remedial fluids that dissolve the contaminant until it is completely removed. For a given flow tube, C_{ej} becomes zero when the volume of injected remedial fluid exceeds $PV_{cj} + 1$ (see Eq. (6)). Remedial fluid injected after that point in time contributes to decreased overall efficiency.

The theoretical short-term benefits, resulting from the injection of a single remedial fluid, are calculated in terms of total-swept-pore-volumes of remedial fluid injected. The total-swept-pore-volume is the product of the average travel time and the injection rate (Enfield et al., this issue). When water is the resident fluid the flux-averaged solution

concentration at time zero is the fraction of flowtubes containing NAPL times the mole fraction of the contaminant in the NAPL times the solubility of the contaminant in water. As a contaminant is completely removed from a flow tube, the fraction of flowtubes containing NAPL decreases, reducing the flux-averaged solution concentration. The post-remediation concentration evaluated after a specific number of total-swept-pore-volumes have been injected into the aquifer would be the concentration after all of the remedial fluid has been displaced from all of the flowtubes, and assuming the remedial fluid displacement process only removes NAPL constituents previously dissolved by the remedial fluid. Thus, the fraction of mass removed includes all mass displaced from the flowtubes plus the remedial fluid solubilized contaminants within the flowtubes. The change in solution concentration is related to the number of flowtubes from which all contaminant was removed, while the change in mass includes all of the mass removed from both partially and totally cleaned flowtubes. Thus, it will appear that more mass is removed than is evidenced in change in solution concentration.

3. Model testing

The models were tested by calculating elution curves and cumulative mass removal for the dissolution of chemicals from two pilot-scale field tests and comparing these curves with observed field results. The tests were performed in hydraulically isolated test cells located in permeable unconfined aquifers underlain by low permeability units. Flow was controlled by the injection and extraction of fluids. The flow pattern in each test was different. One was a line drive and the other a vertical circulation well. The first test was performed at a site contaminated with an LNAPL composed of a complex mixture of compounds. The remedial fluid was displaced through the formation using a line-drive flow pattern. The second test used a series of vertical circulation wells to displace remedial fluid through a formation into which a known volume of tetrachloroethylene (PCE) had been injected.

3.1. Line drive LNAPL cosolvent extraction

The first test was performed at Hill AFB Operational Unit 1. The rationale for including this site was to examine remedial performance under conditions of relatively uniform contaminant distribution and flow patterns that reasonably approximated a one-dimensional system. The site is contaminated with a complex mixture of chemicals dominated by fuels and degreasing solvents. The geology consists of a shallow sand-gravel unconsolidated unconfined aquifer underlain by a thick silty clay. Data from this field test, as well as details of the site, instrumentation and sampling can be obtained from (Rao et al., 1997; Wood and Enfield, 1999). The data utilized in this evaluation are limited to the center extraction well (EW2) because it was least influenced by boundary conditions created by the sheet piles. Remediation was conducted in a line drive configuration from the injection wells to the extraction wells for ten days followed by 20 days of flushing with water. There were times during the study when flow was stopped due to remedial fluid delivery schedules or power outages. These flow interruptions permitted evaluation of

spatial non-equilibrium. The time scale presented is elapsed time for flow. Indicators are shown when there were significant periods without flow. Data collection for target contaminants was terminated when concentrations fell below detection limits. The initial remedial fluid was a mixture of ethanol and water. The ethanol content of this fluid was gradually increased from 0 to 72% (by volume) over a period of 1 day. After holding the injected fluid composition constant for 0.82 days, *n*-pentanol was added to the mixture. The resultant injection fluid contained 65% ethanol, 11.5% *n*-pentanol and 23.5% water. This mixture was injected for 3.15 days followed by 4.35 days of flooding with 70% ethanol, 12% *n*-pentanol and 18% water. The final remedial fluid mixture consisted of 85% ethanol and 15% water and was injected for 1 day before ramping down to water (Sillan et al., 1998). Table 1 shows how the varying remedial fluid composition was modeled. The average flow rates were 3.2 and 3 L/min; the gradient was 0.05 and 0.07; and the viscosity was 1 and 2.16 cp during the tracer experiment and remedial activities, respectively (Wood and Enfield, 1999). The planned injection, model implementation of the injection, measured elution, and projected elution curves for the remedial fluids are shown in Fig. 1. The projected elution curves for ethanol and *n*-pentanol were calculated analytically using superposition based on the previously defined hydraulic structure for three and five populations and the model described in the companion paper (Enfield et al. this issue). The projections were made assuming both ethanol and *n*-pentanol behave conservatively without any retardation. The remedial fluid elution is the basis for projecting remediation. If one is unable to accurately project the delivery of the remedial fluid, it is not possible to accurately project the effect of the remedial fluid on the removal of the contaminants. The projected ethanol curve tracked the observations except when the ethanol was injected at 70%. During most of this time period, the observed effluent

Table 1
Remedial fluid composition used in Hill AFB projections and the estimated solubility of DCB and *n*-decane in the remedial fluid

Remedial fluid	Volume fraction			Estimated solubility (mg/L)		Injection time (days)	
	Water	Ethanol	<i>n</i> -pentanol	1,1-dichlorobenzene	<i>n</i> -decane*	Start	Stop
1	1			1.0E+02	9.0E-02	0	0.125
2	0.84	0.16		4.5E+02	8.8E-01	0.125	0.375
3	0.68	0.32		2.1E+03	8.7E+00	0.375	0.625
4	0.52	0.48		9.3E+03	8.5E+01	0.625	0.875
5	0.44	0.56		2.0E+04	2.7E+02	0.875	1
6	0.28	0.72		9.0E+04	2.6E+03	1	1.86
7	0.235	0.65	0.115	1.2E+05	7.8E+04	1.86	4.43
8	0.18	0.7	0.12	2.0E+05	1.9E+05	4.43	8.79
9	0.15	0.85		3.1E+05	1.7E+04	8.79	10.3
10	0.43	0.57		2.2E+04	3.1E+02	10.3	10.71
11	0.72	0.28		1.4E+03	4.9E+00	10.71	11.11
12	1			1.0E+02	9.0E-02	11.11	

* The solubility of *n*-decane in is 0.009 and 0.089 mg/L deionized water and salt water, respectively but the ionic strength of the salt water was not specified (Verschuere, 1996) 0.09 mg/L was assumed in the calculations. For *n*-decane the chemical where facilitated transport might be important it was included. The concentration of *n*-decane in the water without solvent was Raoult's law based solubility plus 0.08 when NAPL was present.

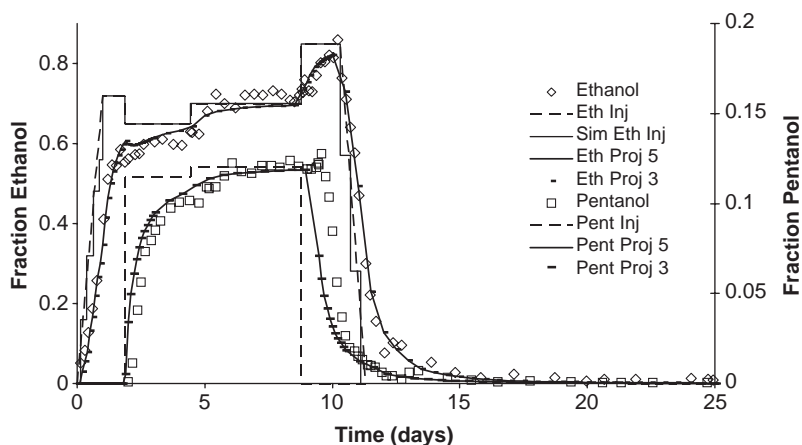


Fig. 1. Hill AFB EW2 plained ethanol and pentanol injections, simulated ethanol injection, measured and projected ethanol and pentanol elution. Projections were made using “structures” for both three and five populations the differences in the projections were typically less than 1%. The model parameters are given in the companion paper. The five population projections are displayed by solid lines and the three population projection curve displayed by the calculated points. The influent ethanol ramps were simulated by a series of step functions as shown.

concentration is greater than the target injection concentration. This discrepancy was not resolved. No significant difference was noted between the use of the three population structure or the five population structure. Both projections are plotted in the figure, but there is no visible difference in the projections. The frontal and distal portion of the measured *n*-pentanol curve appears to have a small amount of retardation. A small amount of retardation of *n*-pentanol would be expected if ethanol were not present, however, significant *n*-pentanol retardation was not expected in the presence of high concentrations of ethanol and retardation of *n*-pentanol was not included in the modelling efforts. Considering variability that occurs under field conditions, and the differences in swept volumes, the projections appear acceptable.

The solubility of an organic pollutant in mixed solvents (\hat{S}_m) has been described by Morris (Morris et al., 1988) as a log-linear function of the volumetric fraction of the cosolvent (f_c) i.e.

$$\hat{S}_m = \hat{S}_w 10^{f_c \beta} \quad (9)$$

For a mixed cosolvent system, Eq. (9) becomes

$$\hat{S}_m = \hat{S}_w 10^{\sum f_i \beta_i} \quad (10)$$

where β is the cosolvency power of the cosolvent and \hat{S}_w is aqueous solubility. Morris states that the cosolvency power can be estimated from the octanol:water partition coefficient and written as

$$\beta = a \log_{10} K_{ow} + b \quad (11)$$

where a and b are empirical constants (for ethanol $a=0.85$ and $b=0.81$ (Augustijn et al., 1997)). Using these numbers one would estimate the cosolvency power of ethanol to be 3.7 for 1,2-dichlorobenzene (DCB) and 5.91 for n -decane. This compares to 4.1 for DCB and 6.2 for n -decane as measured by Dai (1997). Using NAPL from the Hill AFB site Dai reported cosolvency power values for n -pentanol of 3.94 for DCB and 8.87 for n -decane. The cosolvency power reported in the literature is quite variable and considering that this is an exponent in the equation, the uncertainties of estimated solubilities are high.

The NAPL at the site is a complex mixture of organic compounds. Rao et al. (1997) reported the mass fractions for eight of the compounds in the NAPL. The total of the mass fractions reported was 0.024. Thus, much of the composition is unknown. The total fraction for the reported compounds more soluble than 1,2-dichlorobenzene (DCB) or n -decane was 0.00026 and 0.0073, respectively. The solubility of n -decane is very low. It is highly likely that a significant fraction of the NAPL has a solubility greater than n -decane. Without better supporting data on the composition of the NAPL the mole fractions reported by Rao were used to make projections.

Elution curves for two compounds (DCB and n -decane) are shown in Fig. 2. The aqueous solubility of DCB is 100 mg/L ($\log K_{ow}$ is 3.4) and was present in the NAPL at a mass fraction of 0.006 (Rao et al., 1997). DCB observed in the formation fluid prior to remediation was 1 mg/L. This is reasonably consistent with the 0.6 mg/L that would have been expected based on water solubility and mass fraction in the NAPL. The reported mass fraction of n -decane in the Hill AFB NAPL was 0.005 (Rao et al., 1997). Reported aqueous solubilities of n -decane range from 9 $\mu\text{g/l}$ in distilled water to 89 $\mu\text{g/l}$ in salt water ($\log K_{ow}$ is 6.0) (Verschuere, 1996). Computations were made assuming the solubility in the formation water was 0.09 mg/L. However, the concentration observed in the

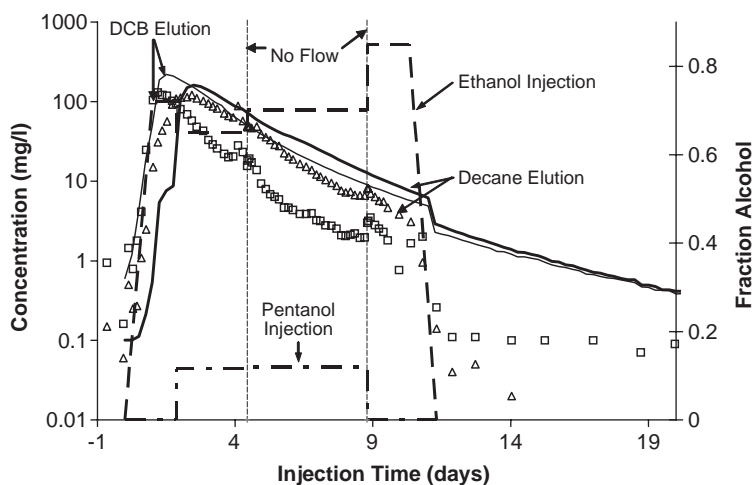


Fig. 2. Measured and projected elution curves for 1,2-dichlorobenzene and n -decane along with target injection curves for the remedial cosolvents ethanol and pentanol. The first flow interruption was for 40 h and the second flow interruption was for 18 h.

groundwater prior to remediation was 0.1 mg/L. Considering the mole fraction of *n*-decane in the NAPL, this is significantly greater than would be expected (0.00045 mg/L). One possible explanation is transport associated with dissolved organic carbon found in the uncontaminated groundwater as described by Enfield et al. (1989); this mechanism will have a much greater impact on *n*-decane than DCB and essentially impacts the *n*-decane when the remedial cosolvents are not present. This mechanism has been included in the projections but not presented in the theoretical development.

Estimated solubilities for DCB and *n*-decane in the remedial fluids are presented in Table 1 along with the assumed remedial program. These solubilities were estimated using Eq. (10) and Dai's values for β from Eq. (11). Predicted and observed DCB and *n*-decane elution curves along with composition of injected remedial fluids are shown in Fig. 2. The predicted elution curves were generated using parameters derived from tracer tests as described by Enfield et al. (this issue). The parameters from the three-population hydraulic structure were used (see Table 4, Enfield et al. this issue). The projections follow the general trends of the data but neither would be called a "good fit". Considering the complexity and lack of knowledge regarding the composition of the NAPL and sensitivity of the cosolvency power of the remedial fluids, the forecasts may be considered acceptable as a screening tool. Since DCB is much more soluble than *n*-decane, one would expect a better fit for the DCB when based on pre-remediation measurements of mole fraction and NAPL saturation. The frontal portion of the DCB elution curve better describes the observed frontal behavior. The model estimates approximately 49 days after the last injection of remedial fluid (the time required for one pore volume to pass through the slowest flow tube) it would be possible to determine the benefits of the remediation assuming flow continued at the same rate. For this elapsed time, both the model projections and field observations were below quantification levels. However, since projected elution concentration were higher than observed concentration during remediation, it is likely that the model underestimates post-remediation contaminant concentrations assuming initial contaminant mass estimates are correct.

3.2. Vertical circulation DNAPL surfactant extraction

The second test was a micellar-enhanced solubilization demonstration performed at the Dover AFB National Test Site (DNST) (Thomas, 1996). The DNST was permitted (Noll et al., 1998) to inject up to 100 L of tetrachloroethylene (PCE), with a water solubility of 150 mg/L and $\log K_{ow}$ of 2.53 (Verschuere, 1996) in double contained test cells (Starr et al., 1992). As described in the companion paper (Enfield et al. this issue) and (Brooks et al., 2002; Wood, 2001), at the time of remediation 77.9 L of PCE were in the test cell.

Surfactants can facilitate NAPL removal through solubilization or mobilization. Increased apparent solubility, as a result of contaminant partitioning into micelles, enhances dissolution of NAPL. Because of their amphiphathic nature, surfactants lower interfacial tensions between water and NAPL which can result in mobilization of previously immobile NAPL. Properties of the surfactant solution will determine if the NAPL is removed primarily by solubilization or mobilization. Because of the potential downward mobilization of the dense PCE, the surfactant solution used in the

DNTS demonstration was designed to maximize solubilization and minimize mobilization.

Other factors that must be considered in the design of the remedial fluid are surfactant sorption onto the formation solids and viscosities of the fluid both with and without dissolved contaminant. Surfactant sorption was a concern from two perspectives. First, sorption removes a portion of the surfactant from active participation in the remedial process thereby increasing the total volume of surfactant required to accomplish remedial objectives. Second, surfactant that is sorbed on aquifer solids can create a sink for partitioning tracers that could be used to determine the quantity of NAPL remaining in the formation following the demonstration.

The addition of a surfactant typically increases the viscosity of an aqueous solution. In addition, laboratory tests have shown that the viscosity of aqueous surfactant solutions can increase substantially in the presence of dissolved PCE. Elevated viscosities reduce the effective permeability of fluids and thereby inhibit the displacement of remedial fluids through the formation. Thus, the surfactant solution used in this demonstration was designed to minimize fluid viscosities and surfactant sorption. The selected remedial fluid was a mixture of 3.3% sodium dihexyl sulfosuccinate (Aerosol-MA[®] or AMA), 3.3% isopropyl alcohol (IPA) and 0.4% CaCl₂. In this mixture at 25 °C, PCE solubility was 42700 mg/L, the viscosity was 1.6 cp, the interfacial tension (Aq/PCE) was 0.1 dyn/cm, and the density was 1.02 g/ml.

In an effort to maximize contact between the remedial fluid and residual DNAPL, a predominantly vertical flow pattern was established using eight wells (41, 44, 45, 45, 51, 54, 55, and 56 (Fig. 1 Enfield et al., this issue)). The wells were screened from approximately 6.4 to 12.5 m below ground surface. Packers were installed over the interval of 10.4 to 11.7 m. The remediation demonstration took place during August and September of 2000. Surfactant initially was injection in an upward flow direction through the vertical circulation wells for approximately 15 days of remediation after which flow geometries were modified to alter remedial fluid displacement patterns. The model currently does not incorporate this complexity and no attempt was made to evaluate model performance beyond the original 15 days of remediation. It is not, therefore, possible to directly evaluate, with field data, the impact of the 15 days of remediation on contaminant flux.

The injection/extraction scheme used in this demonstration created very non-linear flow lines and offers an opportunity to evaluate the performance of the proposed model under truly 3-dimensional flow conditions. Projections of the effluent concentrations of two of the three remedial fluids generated using properties for four a population hydraulic structure as described in the companion paper are shown in Fig. 3. The model reasonably tracks the CaCl₂ elution curve. This suggests that the assumed hydraulic structure is adequate for describing flow in a nonlinear flow field. There were difficulties in maintaining a constant injection concentration of the AMA. There were analytic equipment problems with the field instrumentation, and the methodology for adjusting the AMA concentration was changed during the injection. This problem is evident in the AMA elution curve. The eluted concentration was significantly less, for much of the time, than projected based on target injection concentrations. Even though small amounts of AMA losses were anticipated, the shape of the elution curve is not consistent

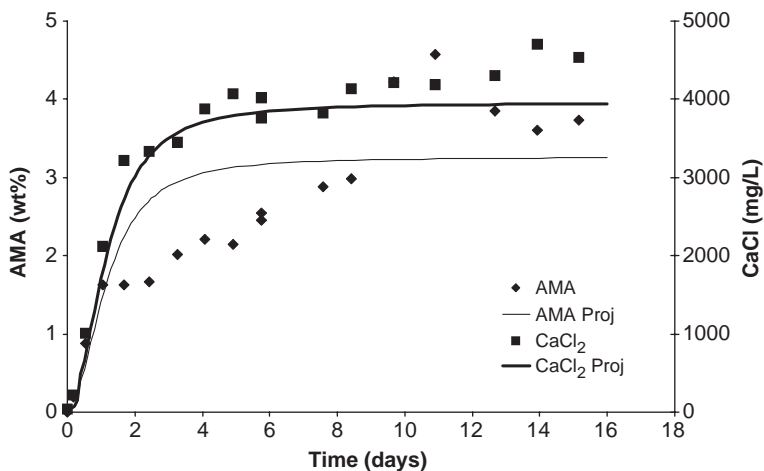


Fig. 3. Measured and projected response to remedial fluids at vertical circulation well 55 Dover AFB National Test Site.

with what would be expected using known loss mechanisms. The poor agreement between measured and projected AMA is most likely related to inadequate knowledge of the injection concentrations.

The experimental remedial performance is shown in Fig. 4 along with a predicted performance. The projections were made based on the target injection concentrations. As indicated earlier, there were problems in the field, and the actual injection concentration is

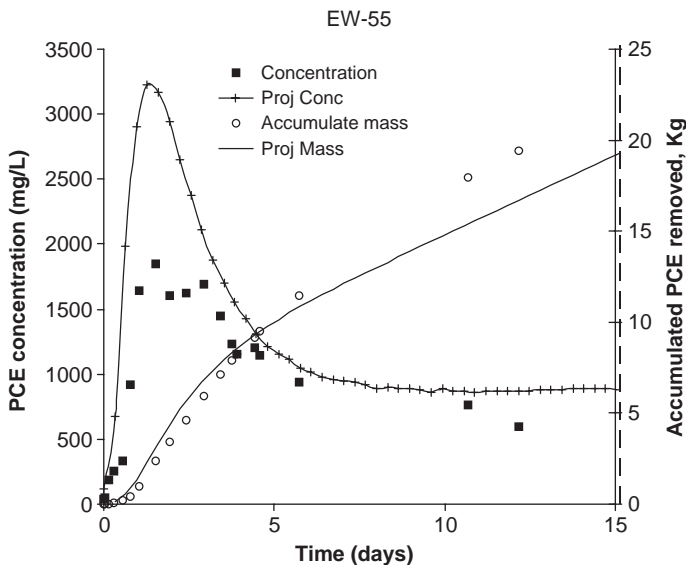


Fig. 4. Measured and projected remedial performance in a vertical circulation implementation of a AMA surfactant extraction.

not known. As stated above, the actual injection concentration is believed to be less than the target early in the study. This is consistent with differences between projected and observed concentrations. Even with the apparent difficulties, the projected accumulative mass removal reasonably follows the measured field values. The model assumed a constant flow (the average flow rate during the 15 days of remediation). Remedial fluid flow variations are the reason for the model projecting less mass removal than observed. A change in direction and extraction patterns prevented an assessment of the impact of DNAPL mass depletion on contaminant discharge.

4. Sensitivity to selected parameters

Eight different architectures describing the distribution of the NAPL were considered in the companion paper (Enfield et al. this issue). Only the architecture providing the “best” fit to the experimental data are discussed above. One could question the fitness parameters that were used to select the “best” architecture since there was no defense of the criteria. A qualitative approach to determine if the selected architecture is appropriate would be to look at the projected elutions for the eight architectures and qualitatively compare the shapes of the projected and observed elution curves (Fig. 5 for the line drive test). There are differences in the shapes. It can be seen that the shapes of some of the curves are consistent with the shape of the experimental curves. None of the projections compare favorably with the magnitude of the observed data. As mentioned earlier, there is a range of literature reported cosolvency powers and for internal consistency the values used in the projections were selected from a single reference. The NAPL composition including the mole fractions of DCB and *n*-decane were estimated from samples taken from a well outside the swept volume of the test and may not be representative of the NAPL properties

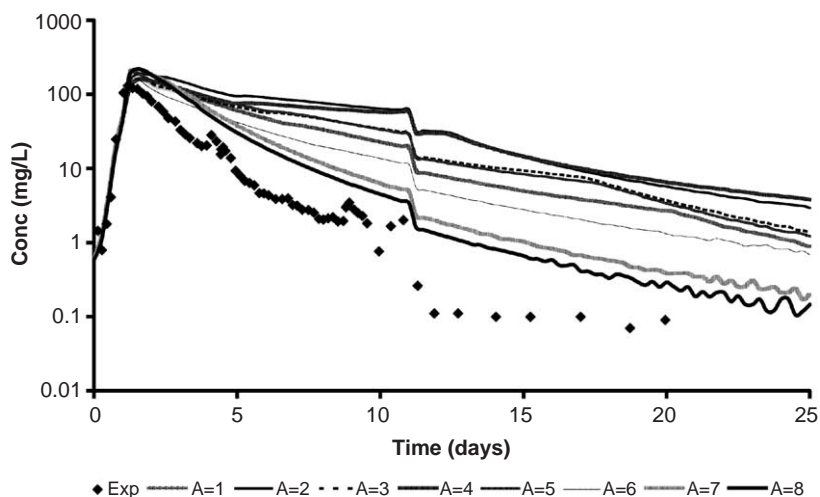


Fig. 5. Measured and Projected Elution curves considering eight potential NAPL architectures. The architecture number refers to the architecture number in the companion paper.

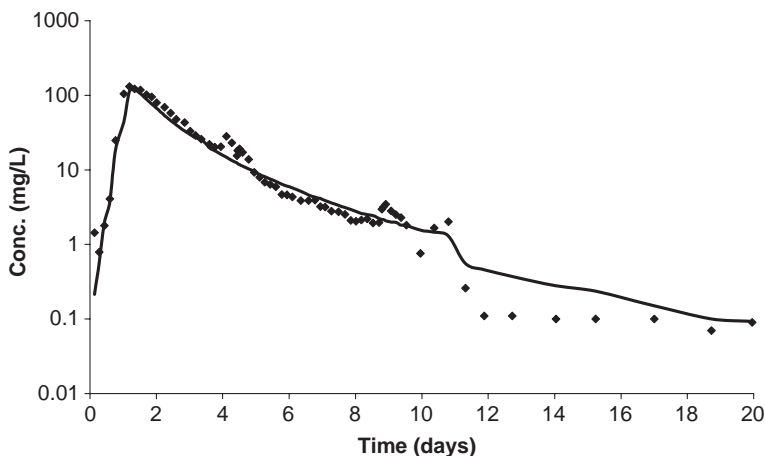


Fig. 6. Calibrated DCB elution projection and field experimental data where the cosolvency powers are 5 and 3.76 for ethanol and *n*-pentanol, respectively and the mole fraction is 0.002.

in the swept volume. It is possible to calibrate the model while maintaining the previously determined hydraulic structure and NAPL architecture to see if other cosolvency powers and mole fraction of contaminant in the NAPL improve agreement between projections and observations (Fig. 6). The calibrated projection closely tracks the experimental data during the cosolvent injection (0–10 days). The discrepancy between observed and predicted behavior during post-remediation water flooding (>10 days) is likely due to differences in viscosities between resident and displacing fluids. These viscosity effects are not adequately accommodated by the model. The model assumes a flow tube is filled with a fluid having the viscosity associated with the eluting fluid. Small errors occur for a short period of time when there are changes in viscosity or gradient. It would be possible to more accurately incorporate viscosity changes but it would be at a computational expense. Since one of the underlying objectives for developing a simplified model is to have a very computationally efficient code, this was not included.

Although not shown in Fig. 6, DCB elution behavior was projected to 60 days. The low concentrations of DCB at the end of the projection period suggest some of the DCB remained after remediation. This is consistent with the core data collected at the end of the experiment (approximately 99% removal) and provides additional confidence in the model projections.

5. Benefits of source removal

A metric often used when evaluating the performance of a remedial system is the amount of mass removed. This is frequently the metric of choice of those performing the remediation because it is easy to measure, and there are typically large uncertainties associated with estimates of initial and final quantities of contaminant within the formation. Regulatory communities frequently want to show that the concentration is

below some threshold value such as the maximum concentration level (MCL) as a pass–fail metric of performance. One could argue that, due to heterogeneity, if all points within the boundaries of a contaminated site must be reduced to below this threshold level, remediation is technically impracticable. This is like saying that if you look hard enough on a small enough scale you will be able to find a location where contamination has not been removed and, therefore, not sufficiently remediated. It may not be critical to remove all of the contamination (Soga et al., 2002). Contamination that is effectively isolated from the flow field does not present the same environmental risk as contamination that is accessible and readily transported under natural gradients. Contaminant flux across a control plane might be a better metric of choice when the objective is to reduce exposure

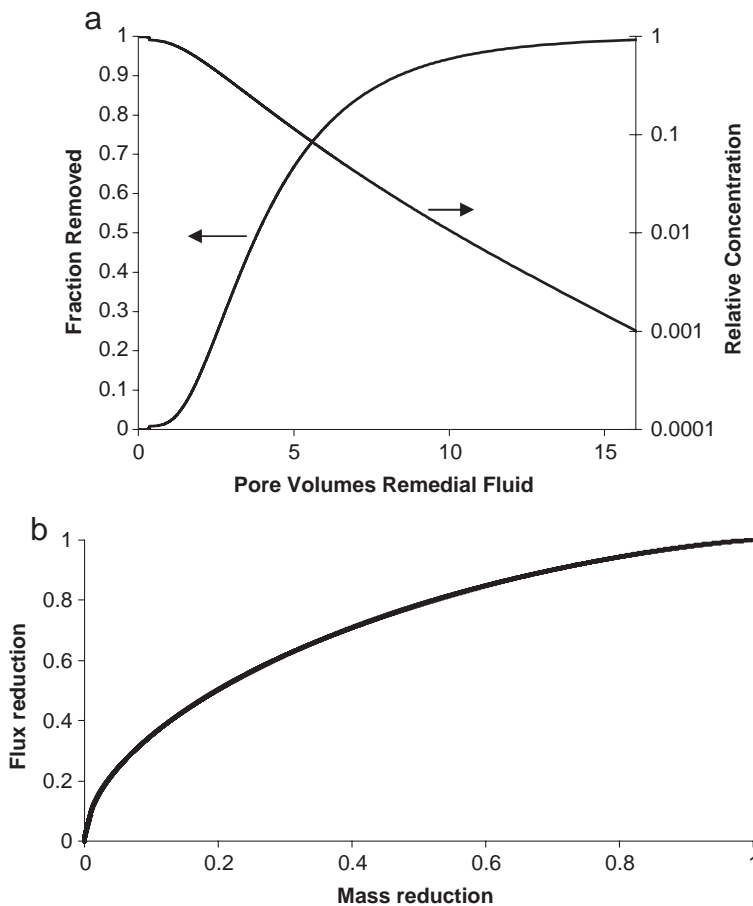


Fig. 7. a. Benefits of remediation in terms of the number of pore volumes of remedial fluid injected. Properties for a three-population model of Hill AFB EW2 were used in the simulation. The solubility of the contaminant in the remedial fluid was assumed to be 64000 mg/L and the mole fraction was assumed to be 0.006. b. Benefits of source zone remediation based on the three-population model of Hill AFB EW2 described in the companion paper (Enfield et al., this issue).

risk to the environmental. Here, benefit will be defined as either a reduction in contaminant mass or a reduction in average mass flux and will be reported in terms of pore volumes of remedial fluid injected passing through the swept volume.

Given the hydraulic “structure” and the NAPL “architecture” of the source zone and relevant properties of the remedial fluid, the Lagrangian stochastic model can be used to predict mass removal for a single remedial fluid as a function of the volume of remedial fluid eluted through the formation. Assumptions used in these predictions include: contaminant removal is via solubilization by the remedial fluid only, and all of the remedial fluid is extracted from the formation before the mass is calculated (this is an idealized solution not what would happen in reality). In a similar manner, one can calculate in an idealized manner the anticipated change in groundwater concentration at the extraction control plane as a function of the number of pore volumes of remedial fluid displaced through the formation. To estimate groundwater concentration following remediation it is assumed that eluant contaminant concentrations from flows tubes containing any residual NAPL are equal to the equilibrium aqueous concentrations as determined by Raoult’s Law (aqueous solubility for single constituent NAPL). In other words, contaminant concentrations from partially cleaned flowtubes do not change. Contaminant concentrations from completely cleaned flowtubes are zero.

Predictions of mass removal and resultant groundwater concentrations for the line drive LNAPL cosolvent extraction are shown in Fig. 7a for a hypothetical chemical with properties like DCB. The mass fraction of the compound in the NAPL was assumed to be 0.006. The assumed solubility of the chemical in the remedial fluid is given in the figure. At zero pore volumes the relative effluent concentration and the mass removal are one and zero, respectively. As remedial fluid is injected, the mass removed increases and the flux-averaged solution concentration decreases. For this projection, to reduce the flux-averaged concentration of the DCB by 90% it would be necessary to reduce the mass of DCB in the formation by 93% and to reduce the flux average concentration by 99% it would be necessary to remove 99% of the DCB mass. The same data can be plotted in terms of mass reduction versus flux reduction (Fig. 7b). From this plot, one would conclude that incremental changes in mass would result in incremental changes in flux.

The predicted benefits of surfactant-enhanced remediation using the vertical circulation wells (shown in Fig. 8) are quite different from the line-drive cosolvent remediation and

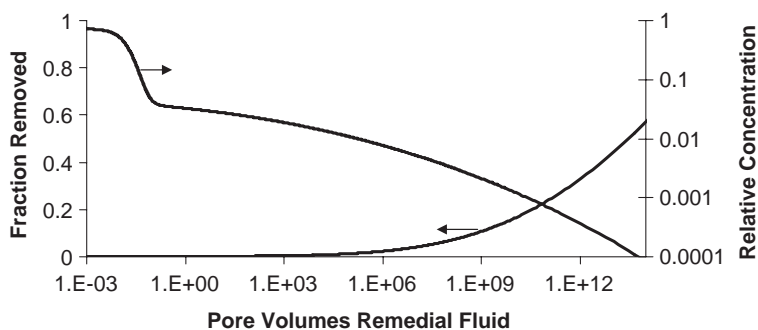


Fig. 8. Benefits projection for the surfactant remediation of PCE contamination using vertical circulation.

the nature of these predicted benefits are dependent on the assumed “architecture” of the NAPL. The relative reduction in flux-averaged concentration is less than 1 at zero pore volumes (not displayed). It is plotted this way to indicate that not all of the fluid that is injected into the formation comes in contact with the PCE. Approximately a log reduction in flux-averaged concentration is predicted with approximately one pore volumes of remedial fluid but very little mass is removed. To get a second log reduction in flux would require a large number of pore volumes of remedial fluid. This would suggest that cost of remediation would be extremely high if more than a log reduction in flux was required to meet remedial objectives but relatively low if only one log reduction were required.

Some have argued that before any benefit (reduction in flux-averaged concentration) is observed most of the mass must be removed (Sale and McWhorter, 2001). Results of the projections for the surfactant enhanced remediation (Fig. 8) are consistent with this hypothesis when more than one log reduction in flux is required to meet remedial objectives. However, in the case of cosolvent-enhanced remediation of the LNAPL source with a different NAPL architecture, substantial reductions in contaminant flux is expected with partial mass removal.

6. Discussion and conclusions

As a simplifying assumption, we assumed that the mole fractions of the contaminants of interest in the streamtubes were initially uniform. This assumption is likely incorrect. The composition will vary dependent on numerous factors including: the number and composition of the releases and the amount of natural weathering that has already occurred. The best we can do with present technology is to obtain samples of the NAPL and determine its composition as it exists today and assume that it is representative of current conditions near the location sampled or infer the composition from the contaminants in the dissolved phase. At large sites the composition is likely to vary from location to location and it may be necessary to take this variability into consideration in forecasting overall remedial performance.

There was a good correlation between model projections and observed remedial elution curves. The complexity of the flow system as illustrated by the vertical circulation flow path did not appear to significantly limit the models ability to simulate remediation. When tracer data is available it can be used to provide the necessary “calibration” for most of the model parameters. When tracer data is not available, similar hydraulic characteristics can be obtained from the soil moisture retention curve using Poiseuille’s equation and scaling the mean travel time (not shown). The fraction of the population that is contaminated can be estimated from the concentration observed in a monitoring well if water solubility of the contaminant of interest and its mole fraction in the NAPL is known. The average residual saturation in the fraction of the flow field that is contaminated can either be estimated based on the physical properties of the NAPL and formation, measured under laboratory conditions or estimated from core samples. Estimates based on this type of data are not likely to produce the level of comparison observed in the figures presented here but may be adequate for an initial feasibility study. The model does not include diffusion. This may not be a problem under the conditions of aggressive remediation but is likely to be

limiting under very low gradients where travel times are long or when there is a large amount of transverse dispersion.

The benefit curves suggest that reducing the flux-averaged concentration down to a level where all environmental concern is removed will be at a considerable resource cost. For architectures that suggest NAPL exists in lenses (near saturation in some of the flowtubes), the volume of remedial fluid required to achieve total cleanup may be extremely large. In some cases, substantial reduction in contaminant flux may be realized with a moderate input of resources. It appears that the correlation between NAPL distribution and hydraulic structure significantly influences the benefit that is achieved from a remedial effort.

The benefits of remediation based on forecasts presented here are quite different than the benefits forecast by Sale and McWhorter (2001). The primary difference is related to the assumptions that are made. Sale and McWhorter assumed that the flow field was homogeneous and the NAPL distribution was heterogeneous. Under the assumptions that the flow field is homogeneous we agree with Sale and McWhorter that essentially all of the NAPL must be removed before a significant reduction is observed in the solution concentration. In this analysis both the flow field and NAPL are assumed to be heterogeneous. If the flow field is heterogeneous, one anticipates the NAPL resident in regions of high hydraulic conductivity is removed quickly and as soon as it is removed the average concentration across a control plane begins to decline. We believe that a limitation of the Sale and McWhorter approach is assuming a homogeneous flow field. A heterogeneous flow field is closer to reality and the benefits predicted using a heterogeneous flow field more accurately reflect what is likely to occur in nature. This does not infer that a heterogeneous flow field is intrinsically easier to remediate. Removal occurs more readily from the more transmissive zones whether by natural dissolution or man induced remediation. If remediation is initiated long after the contamination release, the remaining target contamination may reside in less transmissive regions that are difficult to remediate due to sweep efficiencies. This can be visualized from the projections in Fig. 8. A small amount of the mass was projected to removed quickly. If we assume that this easily removed mass was removed by natural processes prior to active remediation and then active remediation were to begin, it is projected that it would be extremely difficult to get much additional benefit from the removal effort and changes in flux would be slow. The benefits that will be obtained from a remedial effort will depend on: the conditions at the time of the remediation, the ability to deliver the remedial agent to the points of contamination, and remove the impacted contaminant. The approach presented permits estimating the potential benefits of a proposed remediation based on field measurable site specific data.

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