** DRAFT **

A MASS BALANCE APPROACH FOR ESTIMATING DNAPL SOURCE REMEDIATION TIMEFRAME

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ABSTRACT

A mass balance model is developed to facilitate prediction of the relative reduction in remediation timeframe for various DNAPL source treatment alternatives including pump-and-treat, enhanced bioremediation, and surfactant-enhanced aquifer remediation (SEAR). Model simulations reveal that the remediation timeframe for natural dissolution correlates most closely with pool height (which is related to the ratio of surface area to pool volume). A sensitivity analysis demonstrates that source mass depletion and mass discharge reduction are close to a 1:1 relationship in source zones with multiple pools that have a wide variance in pool height. Enhanced in-situ bioremediation is shown to have a relatively small benefit when implemented over a period of only several years. Pump-and-treat, which is often incorporated as a hydraulic containment strategy, is shown to have long-term benefits for source treatment if a relatively high increase in groundwater velocity is maintained throughout the source zone. These results are based on a simplified scenario and are most applicable to aged sources in mildly heterogeneous aquifers.

INTRODUCTION

Chlorinated solvent DNAPLs in groundwater pose a significant problem in North America because of the potential longevity of these sources and the corresponding liabilities that range in the billions of dollars. Emerging research over the past decade indicates that active remediation technologies can result in substantial source mass removal (e.g. up to 90% or higher) at some field sites (Soga et al., 2004). It is recognized that we cannot clean up DNAPL sources completely, and even if we physically isolate these DNAPL sources there may still be lingering mass contributions to aqueous plumes arising because of back-diffusion from low-permeability units (Parker et al., 2008; Chapman and Parker, 2005).

Two challenging questions that should be considered when conducting a feasibility study for DNAPL source treatment are: (1) What will the reduction in remediation timeframe be for a specific source treatment alternative relative to the timeframe for natural dissolution? and (2) How will the implementation of a source treatment alternative affect the mass discharge from the source zone to the downgradient aqueous plume? The answers to these questions depend on the degree of geologic heterogeneity and DNAPL architecture at a site. Due to the challenges in characterizing these features, even expensive computational modeling efforts of remedial performance may have a high degree of uncertainty associated with them.

A number of screening level models have been proposed to estimate the relationship between the source zone mass discharge reduction and the source mass depletion. For example, Falta et al. (2005) propose a relationship similar to

$$\frac{M_d}{M_{do}} = \left(\frac{M}{M_o}\right)^{\beta} \quad (1)$$

where M is the source mass at time t [M], M_o is the initial source mass [M], M_d is the mass discharge from the source zone at time t [M/T], M_{do} is the initial mass discharge [M/T], and β is an empirical fitting parameter. The advantage of predicting how mass discharge and mass depletion are related is that remedial goals for mass removal can be calculated based on a target decline in concentrations or mass discharge in the downgradient aqueous plume. Falta et al. (2005) suggest that β~1 when there is a relatively high ganglia-to-pool (GTP) ratio and there is a positive correlation between DNAPL mass and hydraulic conductivity, and β~*0.5* when mass is predominantly in the form of pools. There are relatively few studies where empirical values of β have been validated. Equation (1) is based on the process of natural gradient dissolution, and does not facilitate the prediction of how active source treatment will influence the remediation timeframe.

The purpose of this study was to develop a simple mass balance screening model that predicts the relative reduction in DNAPL source remediation timeframe for various alternatives involving technologies such as pump-and-treat, enhanced in-situ bioremediation, and surfactant-enhanced aquifer remediation (SEAR). This study outlines the mass balance methodology used in development of the model, and presents an example evaluation of the relative performance of various alternatives for treatment of a pool-dominated DNAPL source zone in a mildly heterogeneous aquifer. The relative remediation timeframe for DNAPL with varying solubility is presented, key source characteristics that influence remediation timeframe are demonstrated, and the β value that may be expected for a zone with multiple pools having a wide variance in pool height is determined.

MODEL DEVELOPMENT

DNAPL Architecture

DNAPL in the saturated zone is typically distributed as vertical ganglia or horizontal pools. Ganglia have a lower saturation and a higher surface area to volume ratio than pools, and thus ganglia will dissolve more quickly than pools (Johnson and Pankow, 1992; Parker et al. 2003; Guilbeault et al., 2005; Parker and Park, 2005). As a result, the time required to remediate a DNAPL source zone will typically be governed by the time to remediate the horizontal pool layers, particularly for aged sources where most of the remaining DNAPL mass is in the form of horizontal layers.

It is proposed in this study that the assessment of partial DNAPL treatment for aged sources in mildly heterogeneous aquifers be focused on the capability of alternatives to enhance pool depletion because:

1. Mass depletion from pools will typically be the driving factor for predictions of remediation timeframe; and,

2. This substantially simplifies the problem given that ganglia in the subsurface are more difficult to characterize because of their heterogeneous (and sometimes apparently random) distribution and their smaller width relative to pools.

Model Development

Johnson and Pankow (1992) present a summary of a pool dissolution analytical model that predicts the aqueous concentration profile and mass discharge from the plume above the pool, based on the processes of advection and dispersion above the pool. To account for the declining rate of mass dissolution from pools due to the reduction in pool length over time, the mass balance model was developed by discretizing each pool source into a series of segments in the direction parallel to groundwater flow. The model calculates the mass dissolved from each pool segment for each time step. When mass becomes depleted in a pool segment, the total length of the pool is adjusted accordingly.

The analytical solution for aqueous concentrations above the pool (modified from Hunt et al., 1988) is

$$C(x_p, z, t) = C_e^t erfc\left(\frac{z}{2\sqrt{D_v x_p / v}}\right) \quad (2)$$

where $C(x_p,z,t)$ is the aqueous concentration at a distance x_p from the upgradient edge of the pool and an elevation z above the top of the pool at time t [M/L^3]; C_e^t is the effective solubility [M/L^3] at time t (and is transient to facilitate the simulation of SEAR-enhanced dissolution); D_v is the dispersion due to molecular diffusion and vertical mechanical mixing [M^2/T]; and v is the average linear groundwater velocity [M/T].

Based on the analytical solution provided by Bird et al. (1960), the mass removed from the pool due to natural dissolution is determined using

$$M_{diss,i} = \left(W_p L_p C_e^t \theta \sqrt{4D_v v/\pi L_p}\right) - M_{diss,i-1} \quad (3)$$

where $M_{diss,i}$ is the rate of mass removed from pool segment i in the current time step as a result of natural dissolution [M/T]; W_p is the pool width [L]; L_p is the pool length in the current time step [L]; θ is the saturated porosity; and $M_{diss,i-1}$ is the mass removed from the upgradient pool segment in the current time step as a result of natural dissolution [M/T].

There is a common misperception that pools typically have a high saturation in the field. Basu et al. (2008) indicate that DNAPL typically has a relatively low saturation in the field (up to 0.25) whereas saturations observed in model simulations or in the laboratory can range up to much higher saturations. As discussed later in this paper, DNAPL saturations in pools up to 36 cm in thickness and situated in sand aquifers above a low-permeability layer will have saturations in the range indicated in Basu et al.. For a DNAPL saturation of 0.25, the relative water permeability in the pool layer may be sufficient to allow for some flow through the pool which would enhance the rate of mass discharge at the downgradient edge of the pool. Figure 1 shows an example where the mass discharge from the aqueous plume above the pool is similar to the mass discharge caused by water flowing through the pool layer. The degree to which water can flow through a pool layer is related to the DNAPL saturation (and corresponding relative water phase permeability), as well as surface topographic features that may limit water flow through pools that sit in a depression in the surface, for example.

The mass balance model for pool dissolution includes an efficiency factor that ranges from 0 to 1 to account for potential mass flux through the pool layer. The rate of mass dissolution from pool segment i in the current time step due to flow through the pool layer ($M_{p,i}$) is calculated using

$$M_{p,i} = \frac{1}{n_p}\left(C_{sol}\, q_p H_p W_p\right) \quad (4)$$

where n_p is the number of pool segments that the pool flux mass is assumed to derive from (and can range from 1, to the number of active segments in the pool); C_{sol} [M/L^3] is the solubility of the contaminant in the DNAPL; q_p [L^3/L^2/T]is the pool specific discharge which is based on the product of the water-saturated specific discharge, the relative water phase permeability, and the pool flux efficiency factor discussed above; and H_p is the height of the pool [L] which is assumed to stay constant over time.

The enhanced rate of dissolution that occurs during in-situ bioremediation is determined using

$$M_{bio,i} = f_{bio}\, M_{diss,i} \quad (5)$$

where $M_{bio,i}$ is the rate of enhanced mass dissolution from the pool due to bioremediation [M/T] in the current time step, and f_{bio} is the enhanced bioremediation efficiency factor. The simulated mass discharge from pool segment i to the downgradient aqueous plume is calculated as the sum of $M_{diss,i}$ and $M_{p,i}$; the mass discharge calculated in the model is assumed to not include any portion of $M_{bio,i}$. The actual mass discharge is expected to be between the value calculated by the model, and the sum of all three mass discharge terms (i.e. dissolution above the pool, flux through the pool layer, and enhanced dissolution due to bioremediation) During simulation of enhanced bioremediation, the focus is more on the change in remediation timeframe and post-bioremediation mass discharge trends, which are not

affected by the simplified mass discharge calculation procedure during enhanced bioremediation. At this time, the mass balance model does not account for daughter-product generation although this may be added in the future.

The total source mass depletion from pool segment i ($M_{out,i}$) during the current time step is given by

$$M_{out,i} = M_{diss,i} + M_{p,i} + M_{bio,i} \quad (6)$$

The mass balance model assumes that multiple pool sources included in a simulation behave independently of each other. The total mass discharge from the source zone is calculated in the model as the sum of mass discharges from each individual pool model included in the simulation. The mass discharge for an individual pool source goes to zero when the mass in all segments of the pool becomes fully depleted during the simulation. The model also uses adaptive time step selection to ensure that the end of a time step corresponds to the time when the next pool segment in the source zone is to be depleted, or the end of the next default time step, whichever comes first.

POOL SATURATION PROFILE ANALYSIS

The mass balance model includes the calculation of average DNAPL saturation in each simulated pool layer based on typical capillary pressure-saturation properties for a sand aquifer, and by re-arranging Equation 3.18 in McWhorter and Kueper (1996) to calculate the effective saturation profile as a function a depth in the pool layer. Figure 2 compares the average saturation profiles for tetrachloroethene (PCE, density of 1600 kg/m^3) and 1,2-dichloroethane (1,2-DCA, density of 1250 kg/m^3), based on the assumption of a residual DNAPL saturation of 15%. Figure 2 demonstrates that the more dense DNAPL will have a higher saturation in thicker pools, and that the average saturation profile is significantly less than may be expected for pools that are up to 36 cm thick.

REMEDIATION TIMEFRAME ANALYSIS

Source Scenario

The purpose of this study is to evaluate simulation results for an aged source zone with multiple pool layers in a mildly heterogeneous aquifer. To conduct this hypothetical simulation, the pool layer areal coordinates defined in an example by Anderson et al. (1992) were utilized. The overall width of the DNAPL source zone was 13.5 metres (m) and the total height was approximately 15 m. The source zone included 12 individual pools. This hypothetical source zone dimension is similar to the width and height of a source zone delineated with a downgradient mass flux transect at a New Hampshire site documented by Guilbeault et al. (2005). At the New Hampshire site, there were 15 concentration maxima on a transect situated 3 metres downgradient of the source zone, and DNAPL was found to occur primarily in thin layers in the aquifer. For this hypothetical simulation, Table 1 presents the initial length, width, height, average DNAPL saturation and Krw, and initial DNAPL mass and volume for each of the twelve individual plumes included in the simulation. TCE is simulated for most of the scenarios discussed below (effective solubility of 1100 mg/L).

Results

The mass balance model is first used to evaluate the pool characteristics that have the strongest correlation with remediation timeframe. Figure 3 shows the correlation between the remediation timeframe of each individual pool, and various pool properties including pool length, width, height, average DNAPL saturation, surface area, and DNAPL volume. The properties with the strongest correlation to remediation timeframe were the average DNAPL saturation and pool height (which are dependent upon each other). The pool height was determined to have a strong influence on the remediation timeframe because this property governed the rate of decline in mass dissolution for each pool. That is, thinner pools had a faster rate of mass dissolution decline because they had the fastest rate of decrease in pool length. This correlation suggests that determining the average pool height is a key feature which should be evaluated for source zones with multiple pools (although it is recognized that

this is a challenging feature to measure in the field). Based on the limited results from this study, it appears that pool height may have more influence on remediation timeframe than the surface area or DNAPL volume, although additional study is needed to confirm this finding.

Figure 4 shows the simulated relationship between source mass depletion and mass discharge reduction for: a) Pool No. 12 which had the thickest pool height in the source zone; and b) the combined source zone behaviour for all 12 pools. The individual pool behaviour is similar to what would be expected given the small reduction in mass discharge for the large initial depletion in source mass. The solid line with symbols shows the overall behaviour for the combined source zone, which appears to correlate with a β value of 0.9 after 35% of the source mass had been depleted. This is different than expected for an individual plume, and indicates that a source zone with multiple pools having a wide variance in pool height behaves similarly to an aquifer with a relatively high ganglia-to-pool ratio.

Figure 5 presents the simulated timeframe for a 90% depletion in source mass for the following natural dissolution scenarios: TCE with pool flux efficiency factors of: 0, 0.1, 0.3, and 1; and 1,2-DCA (solubility of 8500 mg/L) with a pool flux efficiency factor of 0. Figure 5 demonstrates that DNAPL made up of a component such as 1,2-DCA with a relatively high solubility will dissolve much more quickly under natural conditions than TCE. Figure 5 also shows that even a small amount of flux through the pool layer may have a significant influence on the remediation timeframe for pool dissolution when the average DNAPL saturation in the pool is relatively low. During site characterization, it would be advantageous to evaluate the DNAPL saturation profile in pools if possible, and to develop a conceptual model of whether surface topography (e.g. topographic depressions where pools are located) will inhibit groundwater flux through the pool layer.

Figure 6 compares the simulated mass discharge from the source zone for two TCE scenarios (pool flux efficiency factors of 0 and 1). The trends shown in Figure 6 indicate that a large amount of flux through the pool layer will result in a substantially higher mass dissolution rate. If the site is characterized approximately 20 years after the initial release, then the mass discharge rate would be similar for both pool flux scenarios. One may be able to calibrate a mass balance model to the measured rate of decline in mass discharge if other input parameters can be reasonably characterized, although this may be difficult at most sites.

Simulations of three remedial alternatives were conducted using the mass balance model: Case I) Enhanced in-situ bioremediation (EISB) for durations of 1, 2, 3, 5, 10, and 20 years; Case II) EISB for the same durations followed by pump-and-treat for the remainder of the simulation; and Case III) Pump-and-treat only. It is assumed that EISB resulted in a 200% increase in the rate of dissolution (ITRC, 2008), and that pump-and-treat resulted in an average increase in the groundwater velocity of 100% in the source zone. It is assumed that active remediation in each scenario was started at a time of 20 years after the initial release. The remediation timeframes were calculated for each scenario based on a target reduction target of 90% of the mass discharge that was simulated at a time of 20 years (just before the start of remediation). The reduction in remediation timeframe was evaluated to compare the benefits of each alternative, and is calculated based on the reduction in remediation timeframe for each alternative relative to the remediation timeframe for natural dissolution.

Figure 7 compares the relative reduction in remediation timeframe for each alternative. The horizontal dashed line indicates that a pump-and-treat alternative results in a reduction in the remediation timeframe of approximately 27% when compared to natural dissolution. EISB performed for a period of 1 to 10 years resulted in a smaller reduction in remediation timeframe than if pump-and-treat had been performed over the entire operating period. EISB performed for a duration of 20 years had a higher rate of remediation timeframe reduction (42%). Model simulations indicate that if EISB was performed for a period of several years followed by continuous pump-and-treat, then the benefit may be relatively small compared to the pump-and-treat only alternative. EISB would need to be performed for approximately 10 years or more, followed by pump-and-treat, in order to have a significant gain in benefit compared to the pump-and-treat only alternative.

These results are based on a simplified mass balance model that assumes ideal conditions for pool dissolution, that assumes a relatively high increase in velocity due to pump-and-treat, and that does not

take into account potential effects of heterogeneity in the aquifer. Additional study is warranted to verify that this mass balance approach provides a reasonable representation of pool dissolution in mildly heterogeneous aquifers for aged sources, given the purpose of predicting relative changes to remediation timeframe and transient trends in mass discharge from the source zone. Consideration should be given in model construction to the finding that thin DNAPL layers in aged source zones in sandy aquifers may occur in finer-grained deposits (Parker et al., 2003).

REFERENCES

Anderson, M.R., R.L. Johnson, and J.F. Pankow, 1992, Dissolution of Dense Chlorinated Solvents into Groundwater: 3. Modeling Contaminant Plumes from Fingers and Pools of Solvent, Environmental Science & Technology, 26(5): 901-908.

Bird, R.B., W.E. Stewart, and E.N. Lightfoot, Transport Phenomena, John Wiley and Sons, New York, p. 541.

Basu, N.B., A.D. Fure, and J.W. Jawitz, 2008, Simplified Contaminant Source Depletion Models as Analogs of Multiphase Simulators, Journal of Contaminant Hydrology, 97: 87-99.

Chapman, S.W. and B.L. Parker, 2005, Plume Persistence due to Aquitard Back Diffusion Following Dense Nonaqueous Phase Liquid Source Removal or Isolation, Water Resources Research, 41: W12411.

Falta, R.W., P.S. Rao, and N. Basu, 2005, Assessing the Impacts of Partial Mass Depletion in DNAPL Source Zones: I. Analytical Modeling of Source Strength Functions and Plume Response, Journal of Contaminant Hydrology, 78: 259-280.

Guilbeault, M.A., B.L. Parker, and J.A. Cherry, 2005, Mass and Flux Distributions from DNAPL Zones in Sandy Aquifers, Ground Water, 43(1): 70-86.

Hunt, J.R., M. Sitar, and K.S. Udell, Water Resources Research, 24: 1247-1259.

Interstate Technology & Regulatory Council, 2008, In-Situ Bioremediation of Chlorinated Ethenes: DNAPL Source Zones, Case Studies, Washington, D.C.

Johnson, R.L. and J.F. Pankow, 1992, Dissolution of Dense Chlroinated Solvents into Groundwater: 2. Source Functions for Pools of Solvent, Environmental Science & Technology, 26: 896-901.

McWhorter, D.B. and B.H. Kueper, 1996, Mechanics and Mathematics of the Movement of Dense Non-Aqueous Phase Liquids (DNAPLs) in Porous Media, in Dense Chlorinated Solvents and other DNAPLs in Groundwater, Ed. J.F. Pankow and J.A. Cherry, Waterloo Press, Portland, Oregon.

Parker, B.L., S.W. Chapman, and M.A. Guilbeault, 2008, Plume Persistence Caused by Back Diffusion from Thin Clay Layers in a Sand Aquifer Following TCE Source-Zone Hydraulic Isolation, Journal of Contaminant Hydrology, 102: 86-104.

Parker, B.L., J.A.Cherry, S.W. Chapman, and M.A. Guilbeault, 2003, Review and Analysis of Chlorinated Solvent Dense Nonaqueous Phase Liquid Distributions in Five Sandy Aquifers, Vadose Zone Journal, 2:116-137

Parker, J.C. and E. Park, 2004, Modeling Field-Scale Dense Nonaqueous Phase Liquid Dissolution Kinetics in Heterogeneous Aquifers, Water Resources Research, 40: W05109.

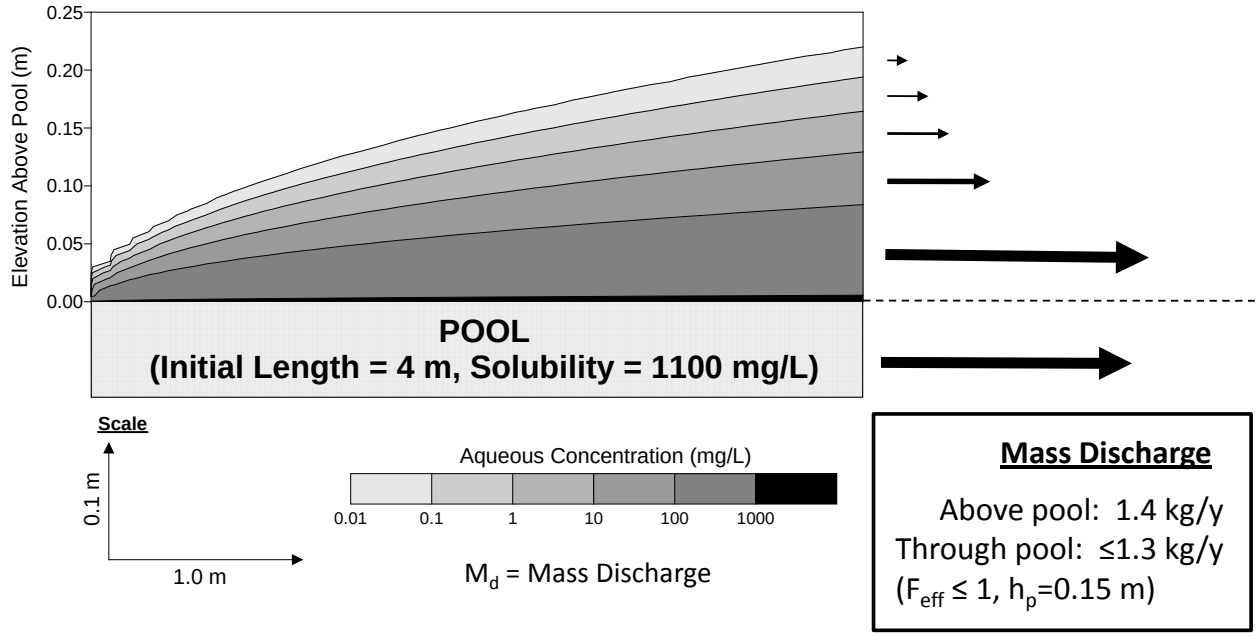

Figure 1 – Conceptual Concentration and Mass Discharge Profiles above a Pool

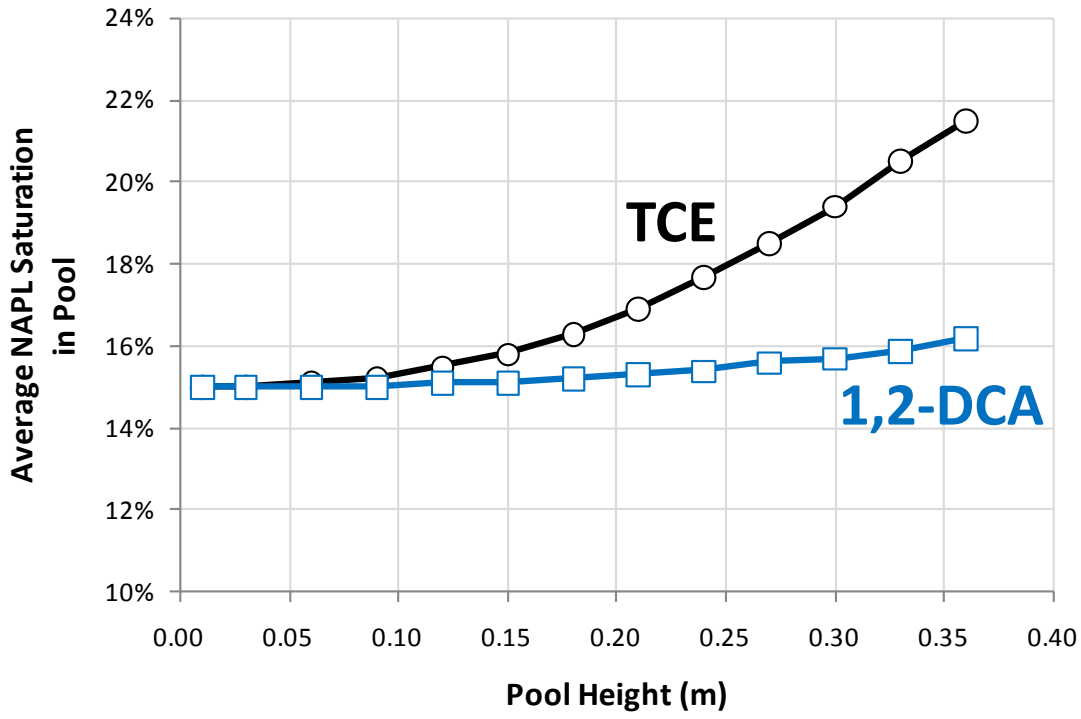

Figure 2 – Influence of DNAPL Density on Average DNAPL Saturation

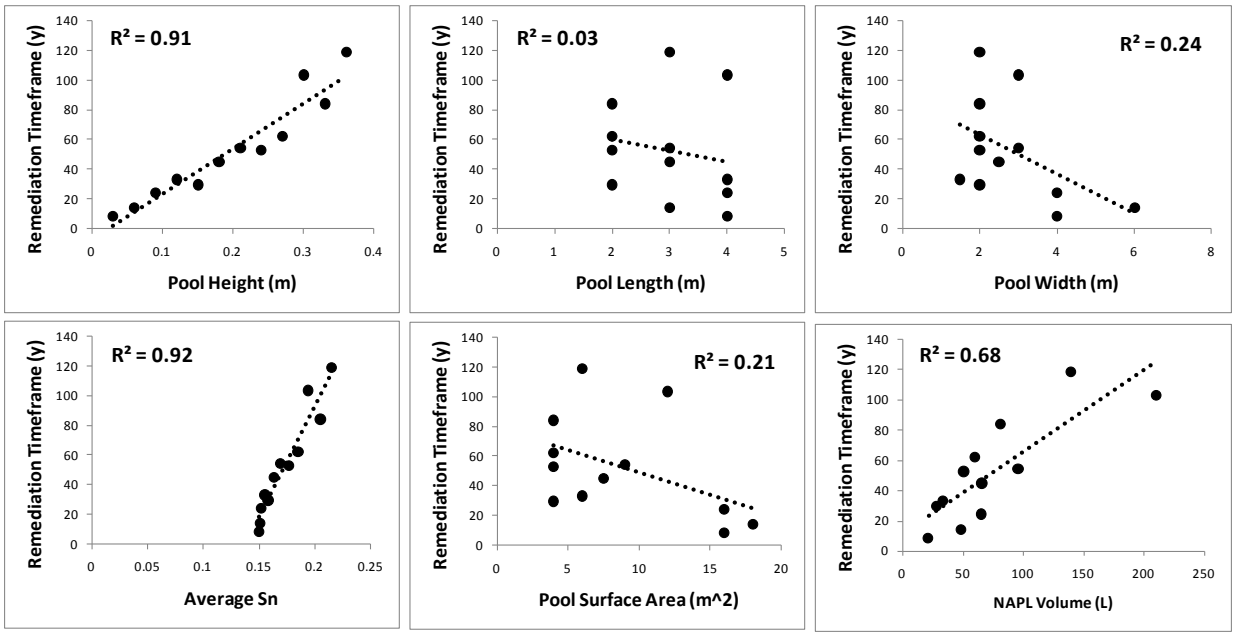

Figure 3 – Remediation Timeframe Correlation with Pool Properties

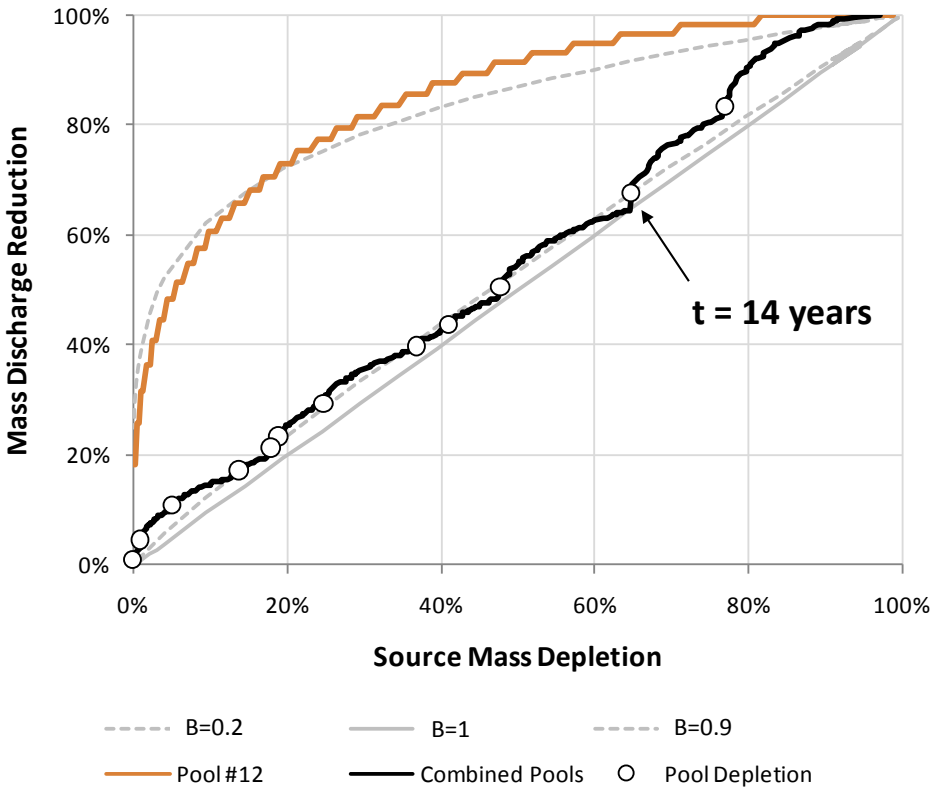

Figure 4 – Mass Discharge Reduction versus Source Mass Depletion

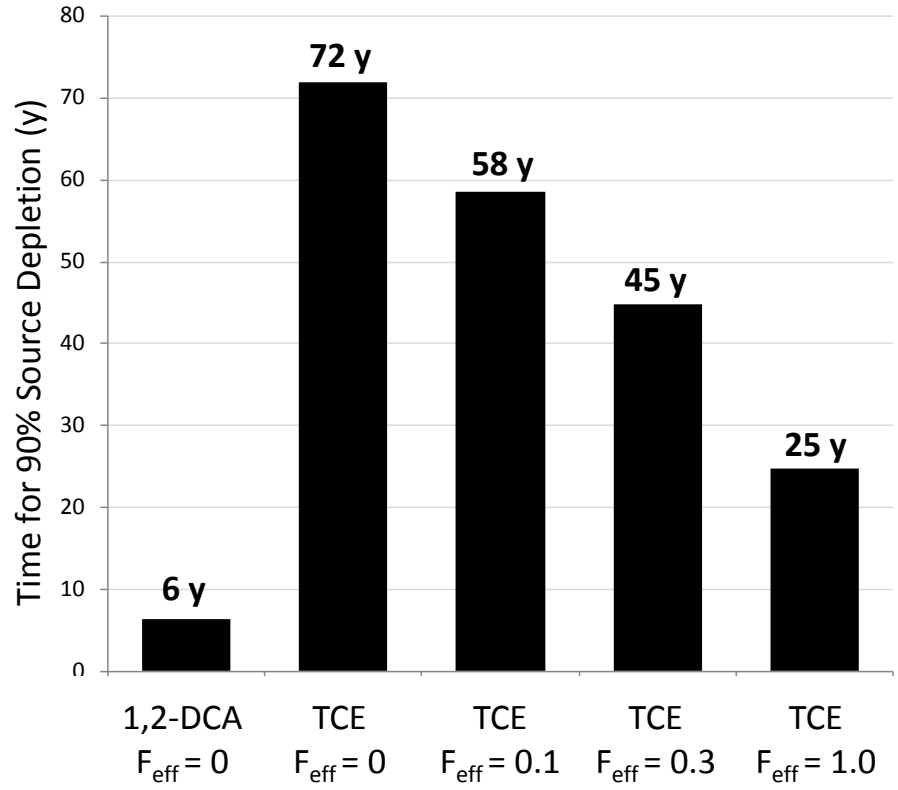

Figure 5 – Predicted Timeframe for 90% Source Mass Depletion

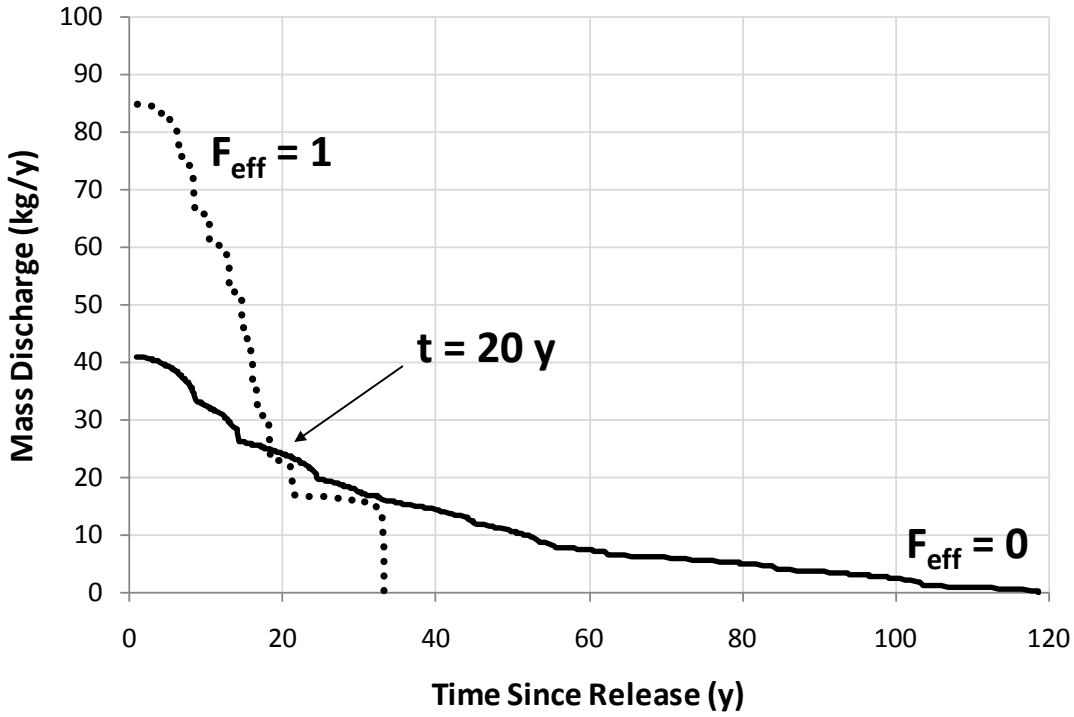

Figure 6 – Influence of Flux Through Pool on Remediation Timeframe

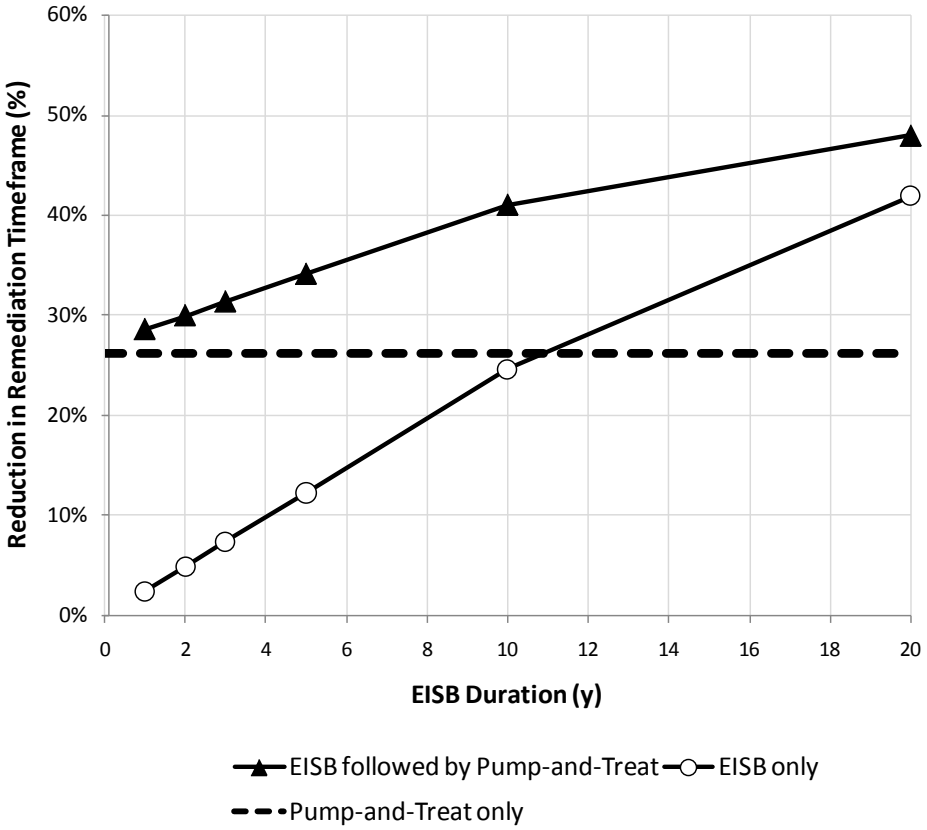

Figure 7 – Comparison of Remediation Timeframe Reduction

Table 1 – Source Pool Characteristics

Pool ID	Pool Height (m)	Pool Width (m)	Pool Length (m)	Average DNAPL Saturation	Average Krw	DNAPL Volume (L)	DNAPL Mass (kg)
1	0.03	4	4	15%	0.27	22	35
2	0.06	6	3	15%	0.27	49	78
3	0.09	4	4	15%	0.26	66	105
4	0.12	1.5	4	15%	0.26	33	53
5	0.15	2	2	16%	0.25	28	46
6	0.18	2.5	3	16%	0.25	66	106
7	0.21	3	3	17%	0.24	96	154
8	0.24	2	2	18%	0.23	51	81
9	0.27	2	2	18%	0.21	60	96
10	0.30	3	4	19%	0.20	210	336
11	0.33	2	2	20%	0.19	81	130
12	0.36	2	3	22%	0.18	140	223