ESTCP
Cost and Performance Report

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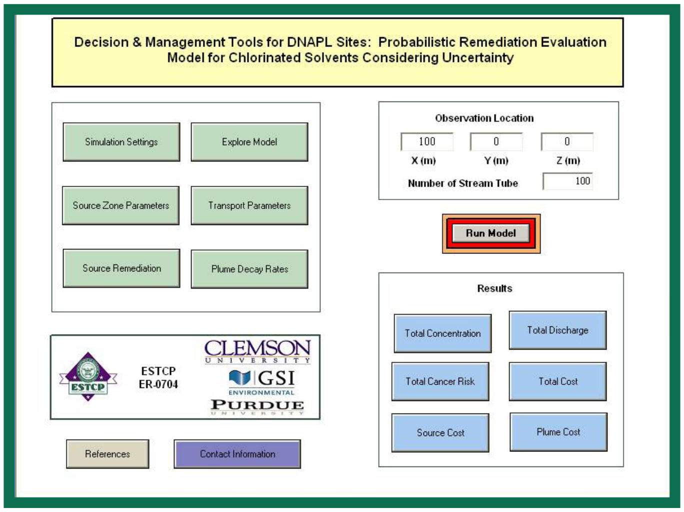

Decision & Management Tools for DNAPL Sites: Optimization of Chlorinated Solvent Source and Plume Remediation Considering Uncertainty

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ACRONYMS AND ABBREVIATIONS

bgs	below ground surface
CVOC	chlorinated volatile organic compound
DCE	cis-1,2-dichlorothylene
DLL	Dynamic Link Library
DoD	Department of Defense
DNAPL	dense nonaqueous phase liquid
ESTCP	Environmental Security Technology Certification Program
GUI	graphical user interface
ITRC	Interstate Technology & Regulatory Council
LB	lower bound
MCL	maximum contaminant level
MNA	monitored natural attenuation
NPV	net present value
NRC	National Research Council
O&M	operation and maintenance
PAT	pump-and-treat
PCE	tetrachloroethylene
PDF	probability density function
PRB	permeable reactive barrier
PREMChlor	Probabilistic Remediation Evaluation Model for Chlorinated solvents
REMChlor	Remediation Evaluation Model for Chlorinated solvents
SERDP	Strategic Environmental Research and Development Program
TCE	trichloroethylene
UB	upper bound
USEPA	U.S. Environmental Protection Agency
VC	vinyl chloride
ZVI	zero valent iron

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1.0 EXECUTIVE SUMMARY

1.1 OBJECTIVES OF THE DEMONSTRATION

The objective of this project was to develop a new probabilistic remediation modeling program, Probabilistic Remediation Evaluation Model for Chlorinated Solvents (PREMChlor), for simultaneously evaluating the effectiveness of source and plume remediation considering the uncertainties in all major parameters, thereby supporting the remediation selection process.

1.2 TECHNOLOGY DESCRIPTION

The technical foundation of PREMChlor is the U.S. Environmental Protection Agency (USEPA) Remediation Evaluation Model for Chlorinated Solvents (REMChlor). REMChlor can simultaneously account for both source and plume remediation. REMChlor includes a source model based on a power function relationship linking the source mass to the source discharge and an analytical plume model based on one-dimensional advection, with three-dimensional dispersion. The plume model simulates natural attenuation or plume remediation temporarily and spatially for parent and daughter compounds in the first-order sequential decay chain. PREMChlor was developed by linking the analytical model REMChlor to a Monte Carlo modeling package, GoldSim, via a FORTRAN Dynamic Link Library (DLL) application. In PREMChlor, all uncertain input parameters are treated as stochastic parameters represented by probability density functions (PDFs). The outputs from PREMChlor are also probability distributions and summary statistics of the distributions. Cost analysis of common technologies for dense nonaqueous phase liquid (DNAPL) source removal and dissolved plume treatment are included. PREMChlor gives users a single platform where cost, source treatment, plume management, monitored natural attenuation (MNA), and risk assessment can all be evaluated together, and where uncertainty can be incorporated into the site decision-making process. A license-free file containing the user-friendly graphical user interface (GUI) has been generated to make PREMChlor available for use by others.

1.3 DEMONSTRATION RESULTS

Model demonstration examples are used to illustrate the different probabilities of meeting a remediation goal for different combinations of source and plume remediation scenarios considering uncertainties in input parameters. PREMChlor has been applied to a trichloroethylene (TCE) plume in a shallow aquifer at a manufacturing plant in Kinston, NC. The calibrated model, using a deterministic approach, closely matched the pre-remediation site condition. Probabilistic simulations predicted the effects of remediation and captured most uncertainties in the key parameters based on estimated PDFs. The PREMChlor model has also been used to conduct sensitivity analyses by assessing the influence or relative importance of each input parameter on plume behavior, in terms of contaminant mass concentration, for three different plume types. Results showed that the degree of influence of different input parameters on the contaminant mass concentration varies widely for different plume types.

1.4 IMPLEMENTATION ISSUES

PREMChlor was developed using an earlier version of GoldSim, so it must be run with GoldSim Player version 9.60. This program is available free of charge from the GoldSim website. The other PREMChlor files are available from the authors.

2.0 INTRODUCTION

2.1 BACKGROUND

The Department of Defense (DoD) is currently responsible for cleanup of groundwater contaminated with chlorinated solvents (chlorinated volatile organic compounds [CVOCs]) at thousands of sites nationwide. Much recent research has focused on technology development for both source and plume remediation (e.g., thermal methods, chemical oxidation, surfactant/cosolvent flooding, soil vapor extraction, air sparging, pump-and-treat [PAT], enhanced in situ biodegradation) (Reddi, 1996; Brusseau et al., 1999; Wiedemeier et al., 1999; National Research Council [NRC], 2000; Kaluarachchi, 2001; USEPA, 2004b; Mayer and Hassanizadeh, 2005; Alvarez and Illman, 2006).

Process and parameter uncertainty and the expensive cost of source and plume remediation efforts have limited our ability to make effective decisions about DNAPL site remediation alternatives. For many sites, a robust, cost-effective remediation design requires some combination of source and plume remediation while considering the uncertainties that arise from hydrological and biogeochemical properties, from the site history and conditions, and from the effects of remediation.

Analytical site modeling tools have played an important role in the remediation selection process. Recently, a new analytical screening level model, REMChlor, has been developed (Falta et al., 2005a, 2005b; Falta, 2008). REMChlor is a significant improvement on existing analytical chlorinated solvent transport models such as BIOCHLOR (Aziz et al., 2000), because it can simultaneously account for both source and plume remediation.

In this project, REMChlor was used as the technical foundation to develop a quantitative decision-making process that allows for quick evaluation of different combinations of source and plume remediation scenarios in the face of uncertainty.

This project was complementary to and made use of knowledge gained from other ESTCP and Strategic Environmental Research and Development Program (SERDP) projects that were focusing on selecting, designing, and evaluating the performance and estimating the cost of DNAPL source remediation.

Unlike many other ESTCP projects, this project does not involve a field demonstration of a particular technology nor is it linked to any specific sites. The final products, PREMChlor software and User's Manual, and this document, therefore, are not site-specific.

2.2 OBJECTIVE OF THE DEMONSTRATION

The overall objective of this project was to develop and demonstrate a new probabilistic remediation modeling program, PREMChlor, that can greatly expand the functionality of REMChlor by using it in a probabilistic optimization framework treatment. PREMChlor gives users a single platform where cost, source plume management, MNA, and risk assessment can all be evaluated together and where uncertainty can be incorporated into the site decision-making process. A license-free file containing the user-friendly GUI has been generated to make PREMChlor available for use by others.

PREMChlor was also tested by applying the model to an actual field site. This demonstration included a sensitivity analysis evaluating the importance of key input variables on the source and plume behavior. The sensitivity analysis was performed by assessing the influence or relative importance of each input parameter on the effectiveness of both source and plume remediation in terms of different plume categories.

2.3 REGULATORY DRIVERS

DoD is currently responsible for managing thousands of chlorinated solvent sites. The CVOCs typically are believed to be carcinogens, and they have low maximum contaminant levels (MCLs) in drinking water. Much recent research has focused on technology development for both source and plume remediation, and there is ongoing debate as to the relative effectiveness of these efforts. This model will help site owners and regulators evaluate the likely performance of source and plume remediation efforts including the effects of uncertainty.

3.0 TECHNOLOGY

3.1 TECHNOLOGY DESCRIPTION

In this project, a new probabilistic remediation modeling program, PREMChlor, was developed. PREMChlor takes into account the uncertainties in all major parameters and allows for quick simulations of different combinations of source and plume remediation scenarios to evaluate remediation alternatives. PREMChlor is developed by linking the analytical model REMChlor to a Monte Carlo modeling package, GoldSim (http://www.goldsim.com/) via a FORTRAN DLL application.

The REMChlor model is the technical foundation of the new probabilistic model. This transport model fully couples the source remediation to the plume remediation. It is not specific to any remediation technology. The contaminant source remediation is simulated as a fractional removal of source mass at a future time after the initial release; plume remediation is modeled by considering time and distance dependent decay rates of parent and daughter compounds in the first-order sequential decay chain (Falta, 2008). The source model is based on a mass balance of the source zone where mass is removed by dissolution and advection with additional decay in the source zone (Falta, 2008):

$$\frac{dM(t)}{dt} = -Q(t)C_s(t) - \lambda_s M(t) \tag{1}$$

where $Q(t)$ is the water flow rate through the source zone due to infiltration or groundwater flow, $C_s(t)$ is the average contaminant concentration leaving the source zone, $M(t)$ is the contaminant mass in the source zone, and λ_s is the first order decay rate in the source zone.

The source mass is linked to the source discharge through a power function relationship to reflect the site architecture (Rao et al., 2001; Rao and Jawitz, 2003; Parker and Park, 2004; Zhu and Sykes, 2004; Falta et al., 2005aFalta, 2008; Parker and Falta, 2008):

$$\frac{C_s(t)}{C_0} = \left(\frac{M(t)}{M_0}\right)^{\Gamma} \tag{2}$$

where C_0 is the flow-averaged source concentration corresponding to the initial source mass, M_0. The exponent, Γ, determines the shape of the source discharge response to changing source mass (Figure 1). When Γ=1, the source mass and source discharge decline exponentially with time (Newell and Adamson, 2005; Newell et al., 2006). When Γ>1, the source is never fully depleted, and the source discharge is always greater than zero. When Γ<1, the source is eventually depleted, and the source discharge equals zero in the end. When Γ=0.5, the source discharge declines linearly with time. When Γ=0, the source discharge remains constant until the source is completely depleted (Falta et al., 2005a; Falta, 2007; Falta, 2008).

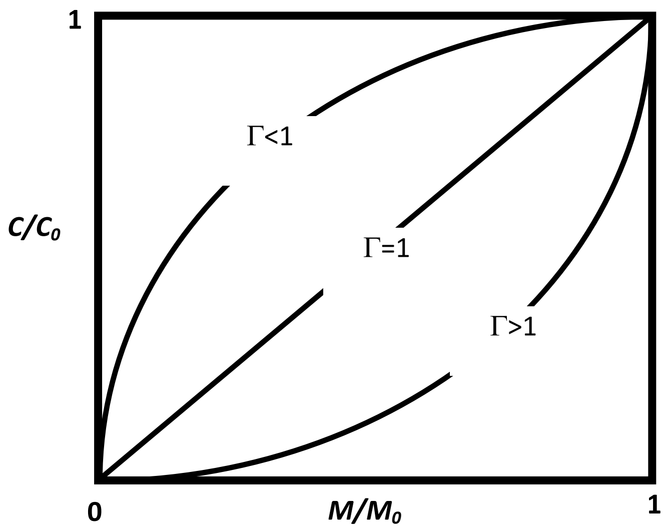

Figure 1. Power function illustration of source mass and source discharge relationship.

Field, laboratory, and theoretical evaluations of the source mass/source discharge response suggest that Γ may vary between about 0.5 and 2 at real sites (Rao and Jawitz, 2003; Falta et al., 2005a; Newell and Adamson, 2005; Fure et al., 2005; Jawitz et al., 2005; McGuire et al., 2006; Newell et al., 2006). Simulation studies suggest that sites with DNAPL located predominantly in low permeability zones exhibit $\Gamma>1$ and sites with DNAPL in high permeability zones exhibit $\Gamma<1$ (Falta et al., 2005a; Falta et al., 2005b). Park and Parker (2005) suggest Γ values greater than 1 for finger-dominated residual DNAPL and less than 1 for DNAPL pools. Essentially, Γ should be considered as an uncertain parameter whose mean value can be roughly estimated but whose actual value may never be precisely known at a site.

The solution of Equation 1 with the power function (Equation 2) can be used to predict the time-dependent depletion of the source zone mass by dissolution. The time-dependent mass is then used in Equation 2 to calculate the time-dependent source discharge. If Q is constant, the solutions are given by Falta et al. (2005b):

$$M(t) = \left\{ \frac{-QC_0}{\lambda_s M_0^{\Gamma}} + \left(M_0^{1-\Gamma} + \frac{QC_0}{\lambda_s M_0^{\Gamma}} \right) e^{(\Gamma-1)\lambda_s t} \right\}^{\frac{1}{1-\Gamma}} \tag{3}$$

$$C_s(t) = \frac{C_0}{M_0^{\Gamma}} \left\{ \frac{-QC_0}{\lambda_s M_0^{\Gamma}} + \left(M_0^{1-\Gamma} + \frac{QC_0}{\lambda_s M_0^{\Gamma}} \right) e^{(\Gamma-1)\lambda_s t} \right\}^{\frac{1}{1-\Gamma}} \tag{4}$$

This source model can account for aggressive source remediation efforts (such as excavation, thermal treatment, alcohol or surfactant flooding, or chemical oxidation) that remove a certain fraction of the source mass over a short period of time (Falta et al., 2005a). By rescaling the equations following the removal of source mass, the source mass and source discharge due to source remediation are presented by Falta et al. (2005b) as:

$$M(t)=\left\{\frac{-QC_2}{\lambda_s M_2^{\Gamma}}+\left(M_2^{1-\Gamma}+\frac{QC_2}{\lambda_s M_2^{\Gamma}}\right)e^{(\Gamma-1)\lambda_s(t-t_2)}\right\}^{\frac{1}{1-\Gamma}} \tag{5}$$

$$C_s(t)=C_2\left(\frac{M(t)}{M_2}\right)^{\Gamma} \tag{6}$$

$$M_2=(1-X)M_1 \tag{7}$$

$$C_2=C_0\left(\frac{(1-X)M_1}{M_0}\right)^{\Gamma} \tag{8}$$

where t_2 is the time when the remediation ends; M_1 is the source mass before remediation; M_2 is the source mass at t_2; and X is the fraction of source mass removed during the remediation. This approach is not technology specific, and it allows for a realistic and mass conservative assessment of the effects of source remediation on source longevity and discharge. The source model serves also as a time-dependent mass flux boundary condition to the analytical plume model.

The plume model considers one-dimensional advection, retardation, and three-dimensional dispersion with first order decay of parent compound into daughter products. The governing equation for the dissolved concentration of each contaminant compound in the plume is as follows (Falta et al., 2005b; Falta, 2008):

$$R\frac{\partial C}{\partial t}=-v\frac{\partial C}{\partial x}+\alpha_x v\frac{\partial^2 C}{\partial x^2}+\alpha_y v\frac{\partial^2 C}{\partial y^2}+\alpha_z v\frac{\partial^2 C}{\partial z^2}+rxn(x,t) \tag{9}$$

where C is the dissolved concentration and R is the retardation factor, α_x, α_y and α_z are the longitudinal, transverse, and vertical dispersivities, respectively; v is the pore velocity; and $rxn(x,t)$ is the rate of generation (+) or destruction (–) of the dissolved compound due to biological or chemical reactions that may vary temporally and spatially. The model considers a parent compound, and three daughter compounds that are produced by first order decay.

A streamtube approach is used to decouple the solute advection and reactions from the longitudinal dispersion. The one-dimensional advective streamtube model is characterized by a constant pore velocity and solute retardation factor. Plume reactions are included in this advective streamtube model. The entire plume is divided into different zones where the reaction rates are time and distance dependent (Figure 2). Cancer risks posed by carcinogenic compounds in the plume are calculated assuming that the contaminated water is used in a house for drinking, bathing, and other household uses (Falta, 2007).

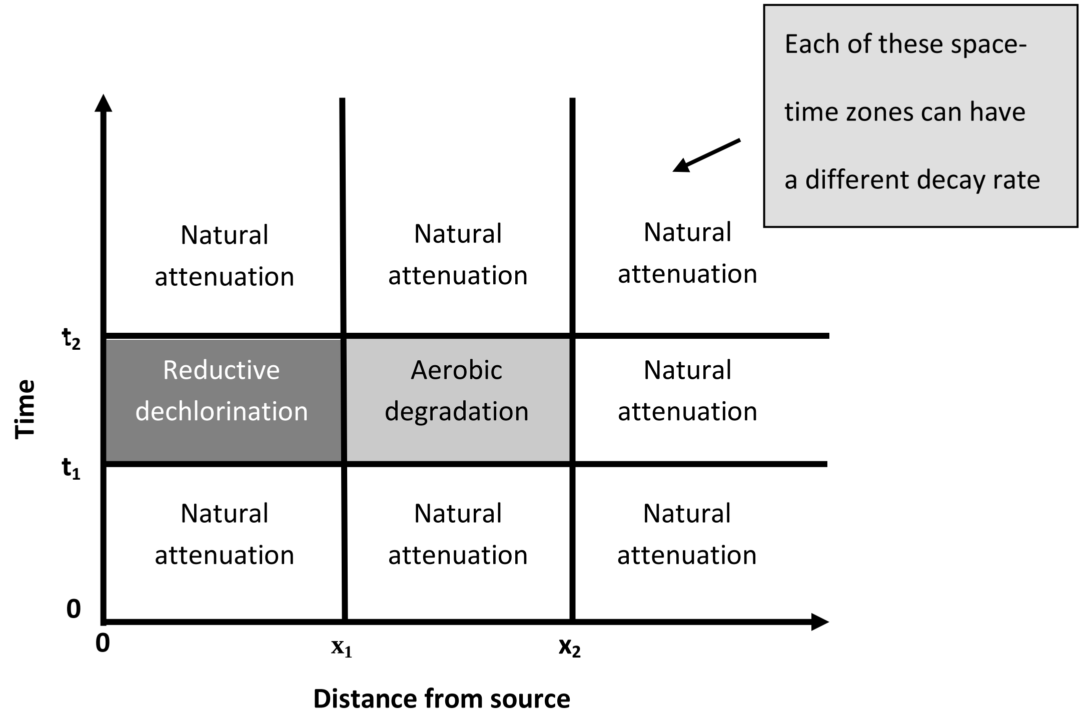

Figure 2. Illustration of plume space-time zones.

By linking REMChlor to the probabilistic simulation package GoldSim, which uses a Monte Carlo approach to propagate the uncertainty in the input parameters of a system to the predicted results and performance, PREMChlor allows all the uncertain input parameters to be treated as stochastic parameters represented by PDFs. The outputs from PREMChlor are also probability distributions and summary statistics of the distributions. Cost analysis of common technologies for DNAPL source removal and dissolved plume treatment are included. PREMChlor gives users a single platform where cost, source treatment, plume management, MNA, and risk assessment can all be evaluated together and where uncertainty can be incorporated into the site decision making process. A license-free file containing the user-friendly GUIs has been generated to make PREMChlor available for use by others.

3.2 TECHNOLOGY DEVELOPMENT

Linkage between REMChlor and GoldSim

Technically, the REMChlor analytical model was compiled as FORTRAN DLL application and then linked to GoldSim. A probabilistic simulation consists of hundreds or thousands of deterministic Monte Carlo realizations. Each realization is an independent and equally likely run of the system. As illustrated in Figure 3, during the probabilistic simulation, GoldSim is used to specify the probability distributions for all stochastic parameters and to specify the Monte Carlo parameters, such as the total simulation duration, time step, and the total realization number for the probabilistic simulation. Inside the Monte Carlo loop, for each realization, GoldSim is used to sample the value for each uncertain parameter through its PDF and specify the value to each deterministic parameter and assign the values to REMChlor. The REMChlor FORTRAN source code is called via a FORTRAN DLL application to perform the analytical calculation, and calculation results are passed back to GoldSim. After all the realizations are completed, all the results of REMChlor calculations are stored in GoldSim and assembled into probability distributions and probability statistics.

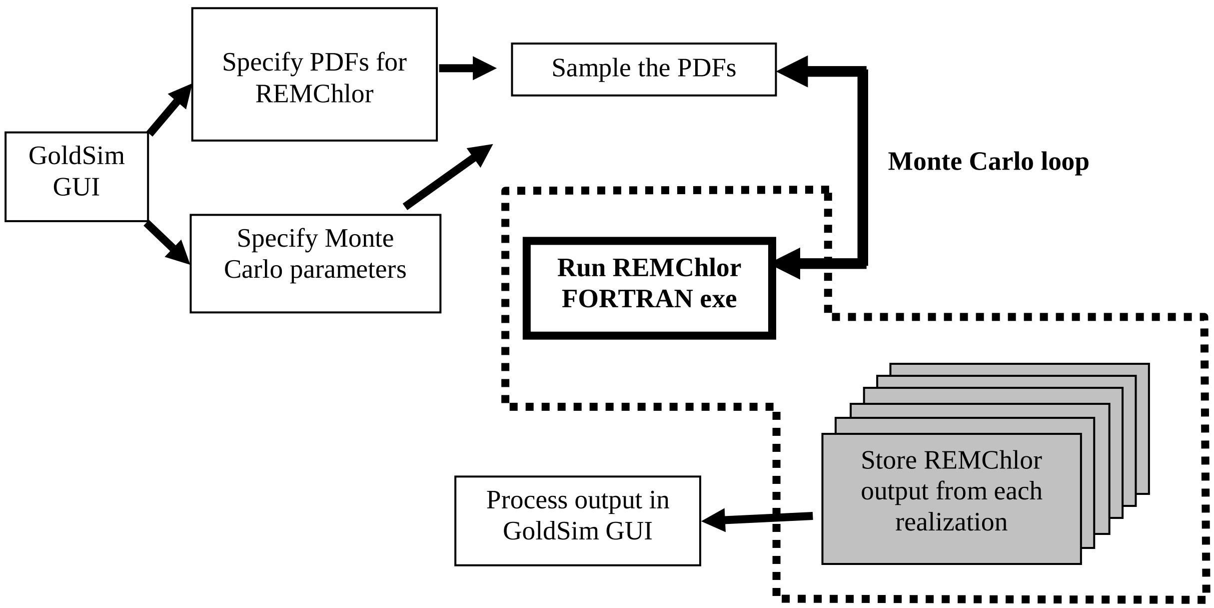

Figure 3. Flow chart of the DLL linkage during the probabilistic simulation.

PREMChlor can be run in two different modes: the probabilistic simulation mode and the deterministic simulation mode. Under the probabilistic simulation mode, model runs multiple realizations. Each realization is deterministic and uses a different probabilistic value for a stochastic parameter. Under the deterministic simulation mode, only one realization is run in which a deterministic value is used for every parameter.

PREMChlor allows two different types of input information, either deterministic or probabilistic values. Deterministic values are provided as the inputs to the model when the user knows the specific values the model requires. When the required information is uncertain, the user provides probability distribution parameters, such as mean and standard deviation as the inputs to define the distribution for a stochastic parameter.

In the PREMChlor model, a GUI has been built to allow other users to easily enter the input values, run the model and view the results. A license-free GoldSim player file containing the GUI has been generated to make the PREMChlor model available to potential users who are not familiar with details of the probabilistic model and the GoldSim simulation environment.

Unit Cost and Remediation Efficiency

PREMChlor considers common technologies for DNAPL source removal and dissolved plume treatment. Source remediation methods include thermal treatments, surfactant/cosolvent flooding, chemical oxidation/reduction, and enhanced bioremediation. The efficiency of source remediation is represented by the fraction of mass removed. In addition, efficiency of enhanced source bioremediation has another option as it can alternately be represented by the enhanced decay rate. In PREMChlor, each remediation technology corresponds to a specific unit cost (cost per volume treated) and specific remediation efficiency. These parameters are treated as uncertain variables represented by the PDFs.

The distributions and the parameters of unit costs and remediation efficiencies were derived from the literature resources. Based on the cost statistic from a comprehensive cost analysis of DNAPL source depletion technologies at 36 field sites (McDade et al., 2005), it was found that the unit cost follows a beta distribution. Based on the statistics of the concentration reduction percentages from a performance evaluation of DNAPL source remediation technologies at 59 chlorinated solvents contaminated sites (McGuire et al., 2006), it was found that the remediation efficiency follows a beta distribution. Due to lack of information, the enhanced decay rate, which is another option to represent the remediation efficiency of enhanced bioremediation, is assumed to have a triangular distribution.

The plume treatment methods mainly are enhanced biodegradation. PREMChlor can also simulate permeable reactive barriers (PRBs). Plume PRB treatment can be modeled by assigning a very high first-order degradation rate for the contaminant in a narrow reaction zone. The application of PREMChlor to a plume PRB treatment can be found in Section 5.2. Due to the lack of information, the unit cost and degradation rate for plume treatment are assumed to have triangular distributions.

Calculation of Remediation Cost

Remediation costs of source removal and plume treatment are included in the probabilistic simulation model. Remediation cost analysis is conducted outside the FORTRAN DLL link. The total remediation cost consists of the source remediation cost and the plume remediation cost. For source remediation, the probabilistic model considers a one-time capital cost, which is the product of the unit cost of the source remediation and the volume of the treated source zone. For plume remediation, cost includes a one-time capital cost and a total operation and maintenance (O&M) cost in present net present value (NPV) for a certain remediation period. The probabilistic model allows two plume remediation zones. For each remediation zone, the one-time capital cost is the product of the unit cost of the plume remediation and the volume of the remediation zone. The calculation of the total O&M cost in NPV is based on the formula in Interstate Technology & Regulatory Council (ITRC) (2006):

$$TotalNPV = \sum_{1}^{n} \frac{AnnualCostinYeartwithInflation}{(1+InterestRate)^{t-1}} = \sum_{1}^{n} \frac{AnnualCost(1+i)^{t-1}}{(1+r)^{t-1}}$$

$$= AnnualCost \sum_{1}^{n} \frac{(1+i)^{t-1}}{(1+r)^{t-1}} = AnnualCost \frac{1-(\frac{1+i}{1+r})^{n}}{1-\frac{1+i}{1+r}} \tag{10}$$

where *AnnualCost* is the current annual cost (assumed to be constant), *i* is the average annual inflation rate, r is the average annual interest rate, *t* is the year, and *n* is the total period of time for plume operation and management. In Equation (10), the numerator accounts for the total O&M cost in current dollars considering inflation, and the denominator accounts for the interest rate. This formula accounts for the inflation and interest factors at the beginning of the second year.

Evaluate and Demonstrate the Model Utility

As presented in four tutorials (see the User's Manual, Appendix D), a hypothetical tetrachloroethylene (PCE) site was modeled to demonstrate the model capability. A series of simulations was conducted and simulation results show the different probabilities of meeting a remediation goal for different combinations of uncertain parameters and remediation efforts. The simulation results are summarized in Table 1.

Table 1. Summary of model demonstration.

Simulation Scenario	Remediation Scenario	Uncertain Parameters	Probability of Meeting a Remediation Goal
Simulation 1	A very effective deterministic thermal remediation of the source that removed 97% of the source mass	N/A	100%
Simulation 2	Identical to Simulation 1, except for adding some uncertainties to the source parameters	• Initial source mass • Power function exponent	>75%
Simulation 3	Identical to Simulation 2, except for making the source remediation efficiency uncertain	• Initial source mass • Power function exponent • Source remediation efficiency	50%
Simulation 4	Identical to Simulation 3, except for adding an enhanced biodegradation of PCE and TCE in the dissolved plume	• Initial source mass • Power function exponent • Source remediation efficiency enhanced biodegradation of PCE and TCE	95%

An example of application of PREMChlor to a real field site is given in Section 5.2 of this report.

The PREMChlor model utility has been evaluated by a test user's group consisting of experts from Noblis, the U.S. Army Corps of Engineers, DuPont Corporation, and Camp Dresser

McKee. Model feedback regarding the general usability and the utility of the model indicates that PREMChlor is functional and user friendly. Model feedback regarding the applicability of the model to the specific sites indicates that PREMChlor is believed to reasonably represent the original contaminant system, and simulation results match field data.

3.3 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

The primary strength of PREChlor is that it allows for quick simulations of different combinations of DNAPL source and plume remediation scenarios to evaluate remediation alternatives while capturing the uncertainties in all major parameters.

PREChlor was developed from REMChlor model; it has the same limitations due to model assumptions (see REMChlor User's Manual, [Falta, 2007]). The primary limitation is that the REMChlor model assumes a simple one-dimensional flow field, and it does not consider diffusion from high velocity regions into and out of low velocity regions.

4.0 PERFORMANCE OBJECTIVES

The performance objectives for this project are listed below in Table 2.

Table 2. Performance objectives.

Performance Objective	Data Requirements	Success Criteria	Actual Performance Objective Met?
Quantitative Performance Objectives			
Develop probabilistic simulation version of the source/plume remediation model with a GUI	• Source containment function • PDFs of unit costs and remediation efficiencies	• Ability to model source containment • Ability to derive the PDFs from literature resource • Ability to link REMChlor to GoldSim	Yes
Apply the model to an actual contaminant site	• Source zone parameters • Transport parameters • Remediation parameters	• Ability to simulate plume • Ability to simulate remediation effort	Yes
Qualitative Performance Objectives			
Evaluate and demonstrate the model utility	• Feedback from usability testing group • Demonstration of model capability	• User friendly graphical interface and applicability to actual sites • Positive reviews from test users group	Yes

Developing the probabilistic simulation software involved the following tasks:

- Task 1 - Modify the current source remediation function in the REMChlor analytical model to include a source containment option.
- Task 2 - Improve the cancer risk assessment calculations in the model to include vapor transport through the vadose zone from a dissolved plume.
- Task 3 - Derive the PDFs of unit costs and remediation efficiencies for remediation technologies.
- Task 4 - Develop a probabilistic simulation version of the source/plume remediation model with a graphical users interface.
- Task 5 - Evaluate and demonstrate the model utility.

The detailed discussions of the technical approach for each task are given in Section 3.2.

The ultimate goal of developing the new modeling tool was to evaluate the field remediation effort in the face of uncertainty. Application of the probabilistic model to an actual TCE site is described in Section 5.2.

Another purpose of this model is to be able to assess the sensitivity of contaminated sites to different remediation actions. Chlorinated solvents source and plume remediation are complex processes due to the many uncertain controlling variables, such as hydrogeological variables, geochemical variables and cost variables. These factors play different roles on the effectiveness of source and plume remediation efforts. Also, the influences of parameters on the effectiveness of remediation for different types of sites are different as well. It is important to explore the influence or relative importance of input variables on the target output (e.g., contaminant mass concentration at a control plane) in terms of different plume types. The site behavior can be divided into three categories in terms of the aqueous plume behavior: a shrinking plume, a stable plume, and a growing plume. For shrinking and stable plumes with the contaminant mass mostly in the source zone, the target output may be mostly sensitive to the removal efficiency of the source treatment. The growing plume is more complicated. For the scenario with the contaminant mass partly in the source zone and partly in the dissolved plume, the target output may be sensitive to the efficiency of both source removal and plume treatment. The sensitivity analysis explores the different importance of input variables to the plume behavior for different types of plumes. More detailed discussions about sensitivity analysis are presented in the Final Report.

5.0 PERFORMANCE ASSESSMENT

The performance objectives of this demonstration included:

- Develop probabilistic simulation version of the source/plume remediation model with a GUI.
- Apply the probabilistic simulation model to an actual contaminant site.
- Explore the importance of key input variables on the source and plume behavior by assessing the influence or relative importance of each input parameter on the effectiveness of both source and plume remediation in terms of different plume categories.
- Through a test user group, demonstrate that the model is useful and reasonably easy to apply.

The results from each are discussed below. Section 5.1 focuses on the model development, Section 5.2 focuses on the model application, and Section 5.3 focuses on the sensitivity analysis. The detailed comments from the test user's group are given in their entirety in Appendix B of the Final Report.

5.1 MODEL DEVELOPEMNT

Detailed discussions about the model development are presented in the PREMChlor User's Guide (Appendix D). This section focuses on the model inputs and outputs.

Among 86 input parameters in the probabilistic model (74 are linked to the FORTRAN DLL), 18 parameters are treated as deterministic and 68 parameters as stochastic. Deterministic parameters usually have less or no uncertainty and can be defined in a certain way. Stochastic parameters are normally associated with much uncertainty. In PREMChlor, four types of distributions, including the triangular distribution, normal distribution, log-normal distribution, and beta distribution, are used for stochastic parameters (Figure 4).

PREMChlor provides many intermediate and final outputs. The most useful final outputs include the concentration and mass discharge of each contaminant component as well as the total values. Contaminant concentration and mass discharge are commonly used metrics to assess the performance of the remediation. In PREMChlor, the changes of concentrations, mass discharges over time (time-histories) are calculated for any specified location (x,y,z). The final results also include the remediation costs. Each output has multiple values computed from different realizations. All these values and observations are assembled into the probability distribution and the probability statistics, including the mean, median, lower bound (LB) and upper bound (UB), and different percentiles (as shown in Figure 5). LB and UB are the lowest and highest values for an output among all of the realizations, respectively. A percentile is the value of an output below which a certain percent of observations fall. Such probability statistics are useful to evaluate the remediation alternatives.

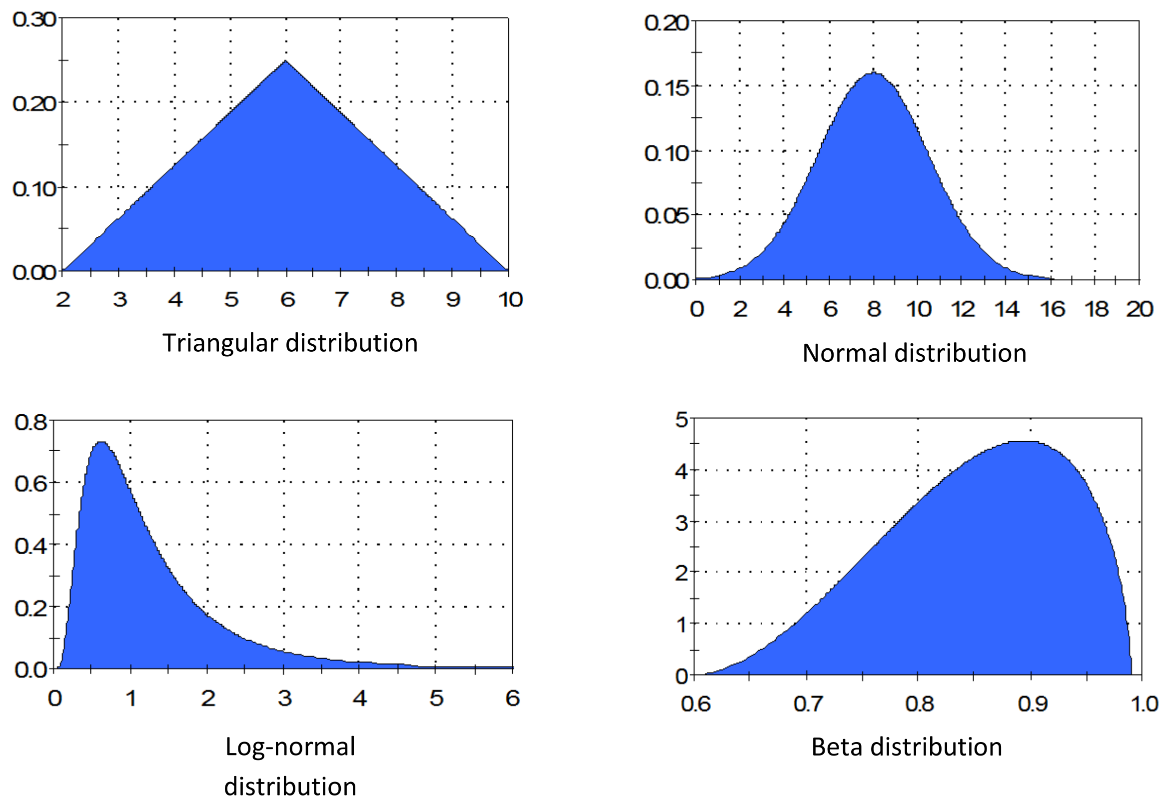

Figure 4. Probability distributions used for input parameters in PREMChlor.

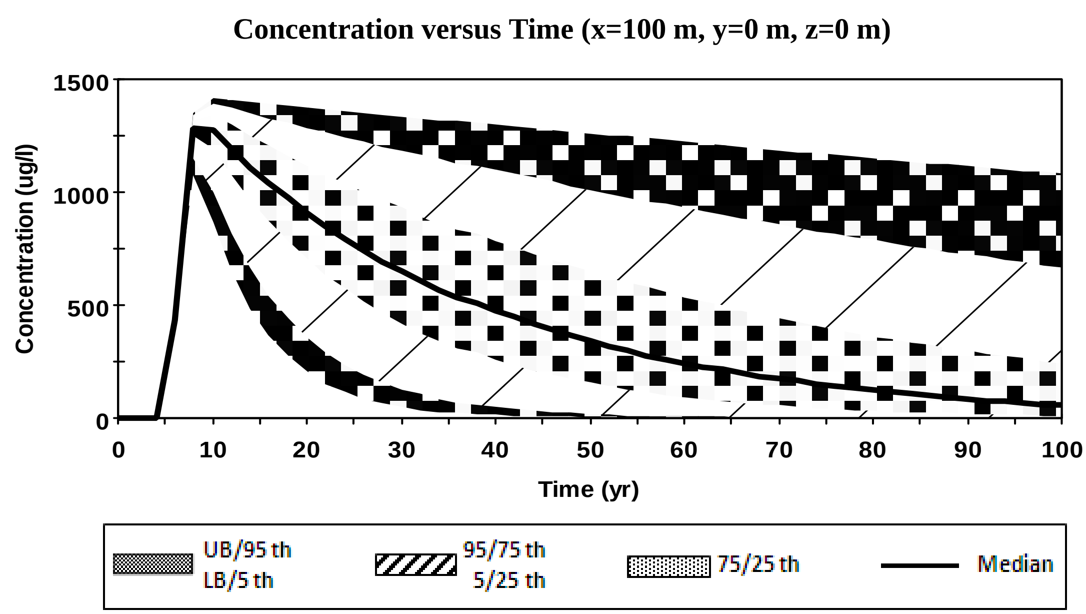

Figure 5. Probability histories of an output.

5.2 MODEL APPLICATION

In this section, the probabilistic model is applied to a shallow aquifer contaminated with TCE at a manufacturing plant in North Carolina. The simulations of field remediation were carried out in two steps. At the first step, the PREMChlor model was calibrated using a deterministic approach to represent the site condition prior to remediation activities. At the second step, the calibrated model was used to conduct the probabilistic simulation of field remediation activities considering uncertainties in seven key parameters. In this step, we pretended to not know the results of field remediation; instead we conducted probabilistic simulation to predict the performance of field remediation efforts.

Site Background and Field Remediation Activities

The site is the DuPont Kinston Plant, northeast of Kinston, Lenoir County, NC. The plant began operations in 1953, and currently manufactures Dacron polyester resin and fibers. In November 1989, site investigation data indicated that the surficial aquifer beneath the manufacturing area had been impacted by a release of TCE. The impacted zone is limited to a surficial sand unit approximately 4.6 m deep overlying a thick mudstone-confining layer. An average hydraulic conductivity for the surficial aquifer is estimated to be 7.7×10^{-4} cm/sec. Groundwater Darcy velocity in the upper aquifer has been estimated to be about 1.52 to 4.57 m/yr. The regional groundwater flow direction is from southeast to northwest, with a pore velocity ranging from 5.56 to 11.13 m/yr. The water table is located at about 1.5 m below ground surface (bgs).

TCE is the main contaminant at the Kinston site. The suspected source region was estimated to be 7.6 m in diameter and to contain about 136 kg of TCE (Figure 6). The aqueous concentration of TCE in the source area showed large fluctuations over time, ranging from 0.34 mg/L to 75 mg/L. Originating from the source zone, the TCE-impacted groundwater plume extended approximately 300 m in the downgradient (northwest) direction, with a width of roughly 76 to 91 m at a downgradient distance of 89 m.

In order to clean up the site, three remediation efforts have been conducted since 1995. Initially a pump-and-treat system was installed to recover and treat TCE-impacted groundwater, resulting in a TCE mass extraction of 3 lb (1.36 kg) during a operation from 1995 to 2001, In 1999, an in situ source area destruction pilot (a reductive dechlorination of TCE) using zero valent iron (ZVI) was conducted to destroy source zone soil contamination. In the meantime, this source ZVI treatment was implemented with a 400-ft-long PRB wall, which was emplaced across the groundwater plume approximately 89 m downgradient of the source area to intercept and treat contaminated groundwater (Figure 6). ZVI was injected into PRB wall to destroy contaminant.

Calibration of the Pre-Remediation Condition

The purpose of this model calibration was to use a deterministic simulation approach to match the site conditions in 1999 prior to source ZVI treatment or plume PRB wall installation.

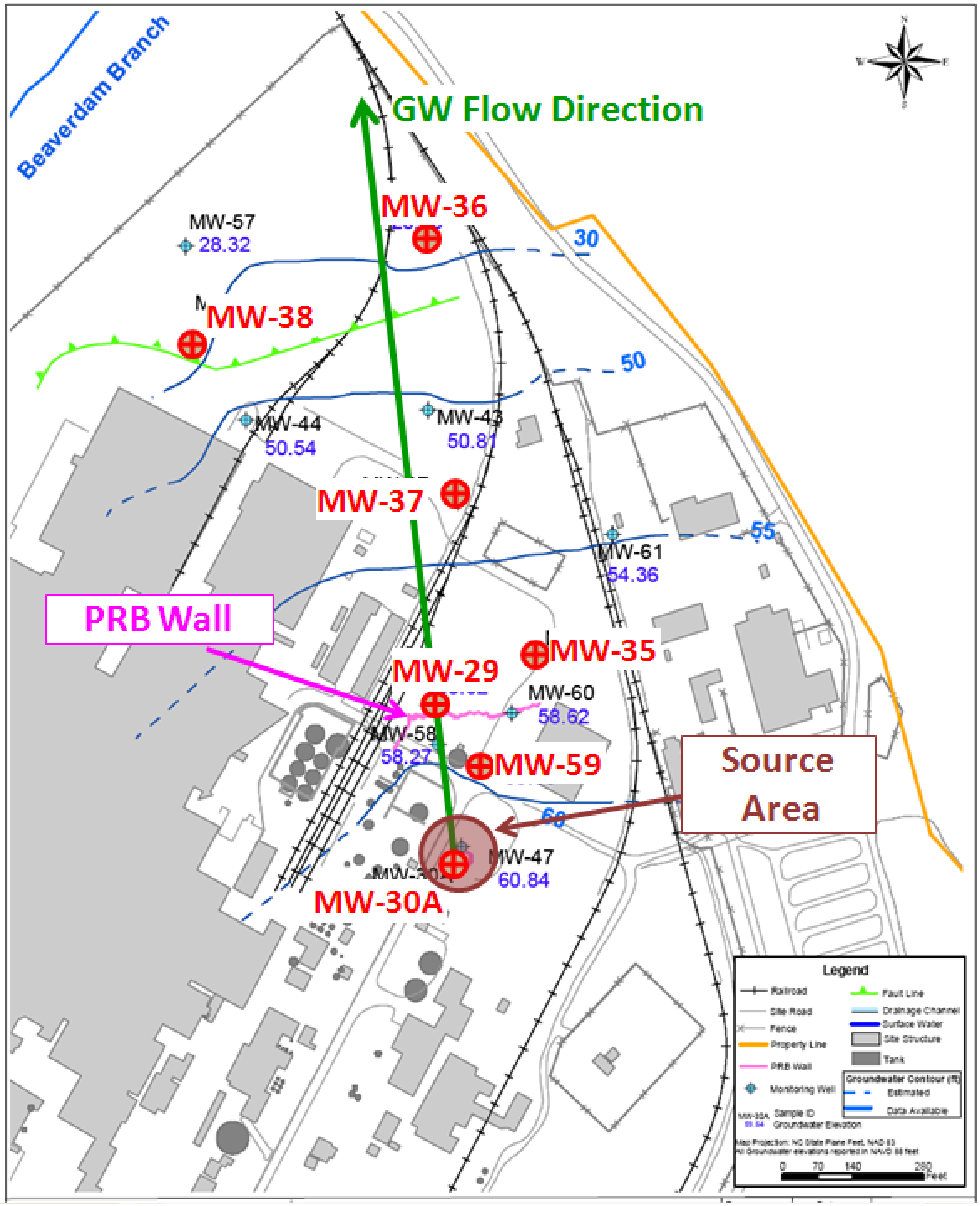

Figure 6. Site map of Kinston plant with monitoring wells.

Because TCE is the major contaminant, the model calibration focused on the TCE plume. To better represent the site conditions, the monitoring well sampling data that are variable both in space and time were used to compare with the simulation results. To be more specific, the simulated and measured time series of TCE concentrations were compared for several monitoring wells sited in different locations in the source zone and plume (see Figure 6). During model calibration, the probabilistic model was set to use deterministic values for all parameters. Some parameters were assigned values that fall in the reported ranges from previous site investigations, some were estimated, and some were calibrated to better match the site conditions. Source, transport, and natural attenuation parameters used in model calibration are shown in Table 3.

Table 3. Source, transport, and natural attenuation parameters used in model calibration.

Parameter	Value	Comment
Initial source concentration, C_0 (mg/L)	6	Estimated
Initial source mass, M_0 (kg)	136	From site reports
Power function exponent, Γ	1	Estimated
Source width, W (m)	8	From site reports
Source depth, D (m)	3.5	From site reports
Source decay rate (yr^{-1})	0	Estimated
Darcy velocity, V_d (m/yr)	8	Calibrated; reports had estimated 1.5 to 4.6 m/yr
Porosity, ϕ	0.333	Estimated from reported Darcy velocity and pore velocity
Retardation coefficient, R	2	Estimated
Longitudinal dispersivity, α_x	x/20	Calibrated
Transverse dispersivity, α_y	x/50	Calibrated
Vertical dispersivity, α_z	x/1000	Estimated
TCE plume natural degradation rate, λ (yr^{-1})	0.125	Calibrated (equal to $t_{1/2}$ of 5.5 yrs)

After model parameters have been estimated or calibrated, the probabilistic model was run in a deterministic way to match the site condition prior to source ZVI treatment or plume PRB wall installation. The comparison of the historical time series of TCE concentration from 1989 to 1998 between the calibrated simulation results and the historical field sampling data for several monitoring wells is shown in Figure 7. Given the facts that 1) the compared monitoring wells are located in different locations in the source zone and plume over a large area and 2) the compared time series of TCE concentration covered a period of time from 1989 to 1998, the agreement of time series of TCE concentration between modeled results and field sampling data in monitoring wells MW-29, MW-35, MW-37, and MW-36 show that with the given combination of parameters as discussed above, the calibrated model with a relatively simple flow field is able to match the pre-remediation site condition in terms of time series of TCE concentration.

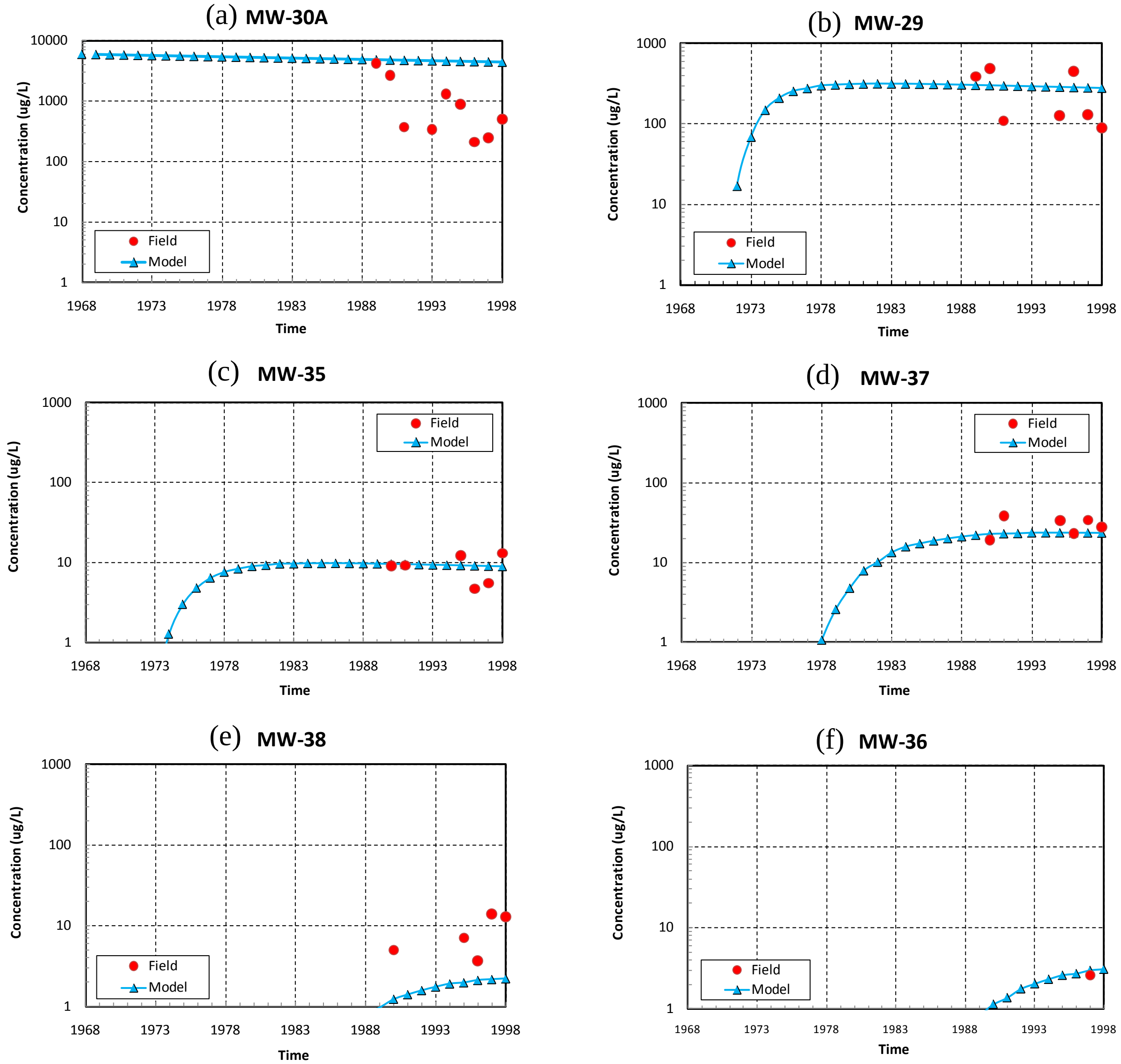

Figure 7. TCE concentrations from model calibration.

The discrepancy of the TCE concentration in the source well MW-30A is probably caused by the initial source concentration used in the model. There is large uncertainty associated with this value. The disagreement of the TCE concentration in the plume well MW-38 suggests that the initial source concentration might be too high or the TCE plume natural degradation rate might be too low. The TCE natural degradation rate used during the model calibration is an averaged estimate for the entire plume. Because the plume is heterogeneous in terms of the TCE degradation rate, this averaged estimate is also associated with some degree of uncertainty. The uncertainties in other transport parameters could also cause such concentration inconsistency for MW-38. There are likely to be other possible combinations of parameters that could match or represent available well data. To capture the uncertainties of these parameters, the probabilistic simulation of field remediation activities were conducted and are presented in the next section.

Probabilistic Simulation of Field Remediation Activities

Based on the previous calibrated model, probabilistic simulations are conducted to model both the source ZVI treatment and plume PRB treatment in order to evaluate the effectiveness of field remediation efforts by considering the uncertainties in parameters. Source ZVI treatment is modeled by removing a fraction of TCE mass from the source zone in a period of 11 months starting from 1999. The plume PRB wall is modeled by assigning a very high first-order degradation rate for TCE in a narrow reaction zone (as shown in Figure 8). The reported effective thickness of the PRB wall is about 10 to 15 cm, so the PRB treatment zone starts from 89 m and ends at 89.127 m in the model.

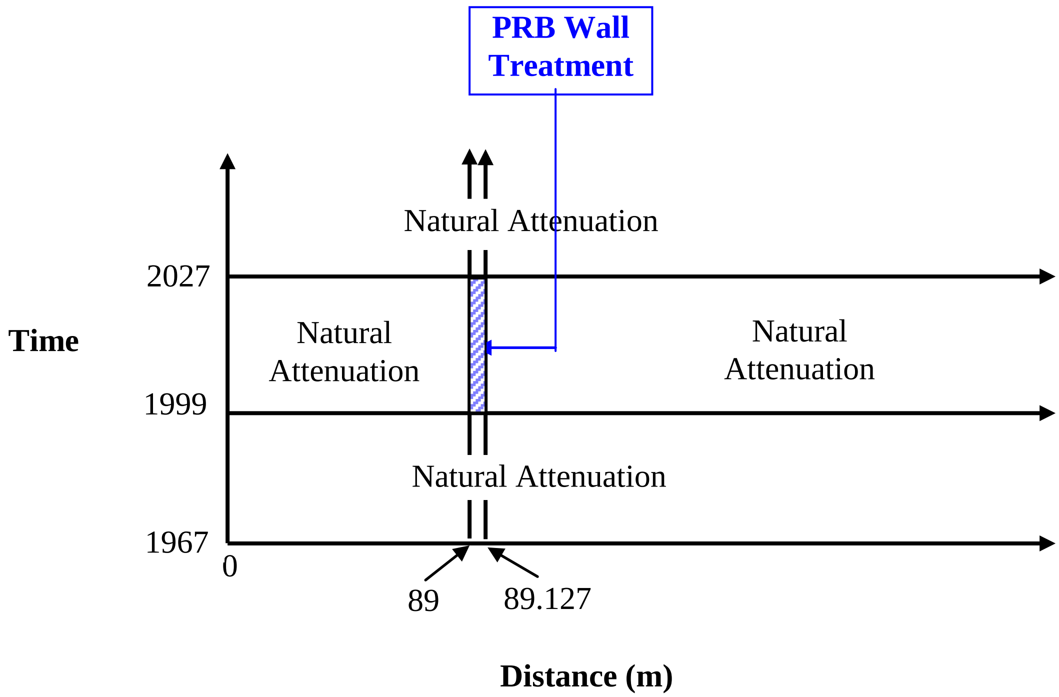

Figure 8. Plume reaction zones, including the PRB wall, modeled in probabilistic simulation.

For this site, seven key parameters, including the initial source concentration, initial source mass, power function exponent, groundwater Darcy velocity, TCE plume natural degradation rate, source mass removal percentage, and the TCE degradation rate inside the PRB wall, are associated with a high level of uncertainty, and they are treated as uncertain variables during the probabilistic simulation. All other parameters are kept as deterministic as in the model calibration. For the uncertain parameters, their mean behaviors stay consistent with the values used in model. The distributions and values of uncertain parameters are shown in Table 4 and the PDFs of distributions are shown in Figure 9. More detailed discussions about model parameters are presented in Liang (2009).

Table 4. Uncertain parameters used in probabilistic simulation.

Parameter	Distribution	Value
Initial source concentration, C_0 (mg/L)	Triangular	min=2, most likely=6, max=10
Initial source mass, M_0 (kg)	Triangular	min=50, most likely=136, max=222
Power function exponent, Γ	Log-normal	geo mean=1, geo stdv=2
Darcy velocity, V_d (m/yr)	Normal	mean=8, stdv=2.5
TCE plume natural degradation rate, λ (yr^{-1})	Triangular	min= 0.05, most likely=0.125, max=0.2
Fraction of source mass removal	Beta	mean=0.85, stdv=0.08, min=0.6, max=0.99
TCE degradation rate inside PRB wall, λ_{PRB} (yr^{-1})	Triangular	min=228, most likely=436, max=644

For each realization, the model simultaneously sampled different values for the seven uncertain parameters and used deterministic values for other parameters. The simulated TCE concentrations are assembled into the probabilistic statistics and are shown in Figure 10. The result of the probabilistic simulations suggest that both source ZVI injection and plume PRB wall installation have affected the TCE concentrations at the Kinston site. Simulation results of monitoring wells MW-30A and MW-59 show that TCE concentration reductions have occurred since the source ZVI injection was implemented, although the data are noisy. Simulation results of the monitoring wells MW-29, MW-35, and MW-37 show the TCE concentration reductions as a combined effect due to both source ZVI injection and plume PRB wall installation. Simulation results of the monitoring wells MW-38 and MW-36 show the remediation efforts will take effect sometime after 2011.

In summary, given a good understanding of the field hydrogeology and biogeochemistry, the calibrated model with a relative simple flow field is able to closely match the pre-remediation site condition in terms of time-series of TCE concentration for a large area of the contaminated site and a relative long period of time. Probabilistic simulations without calibration predicted the effects of remediation and captured most uncertainties in key parameters based on estimated PDFs.

The Final Report for this project contains a parameter sensitivity analysis for three types of plumes: a stable plume connected to a DNAPL source; a growing plume that is disconnected from the source; and a growing plume that is connected to the source. The most sensitive parameters differ widely between cases, depending on the plume characteristics.

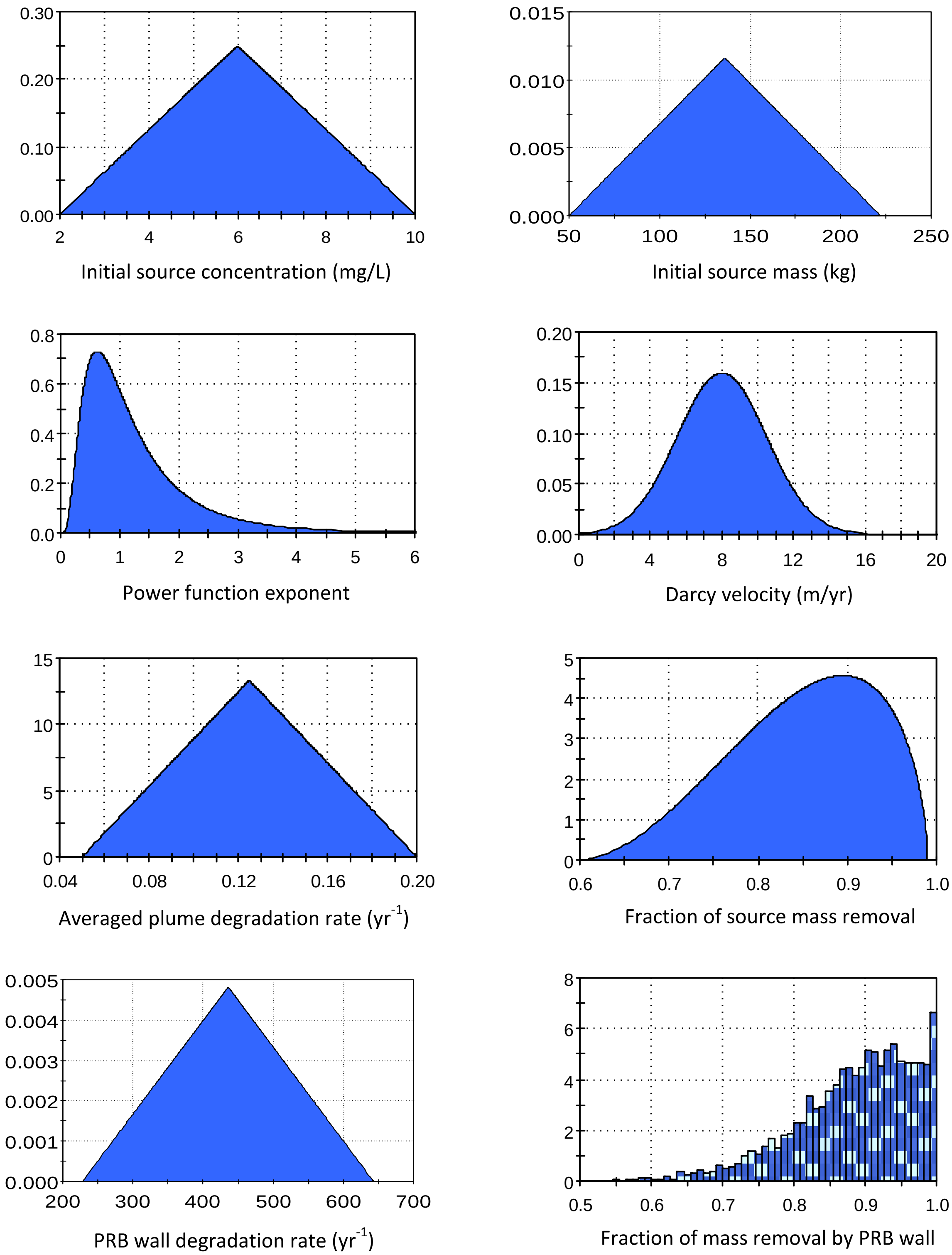

Figure 9. PDFs of uncertain parameters used in probabilistic simulation.

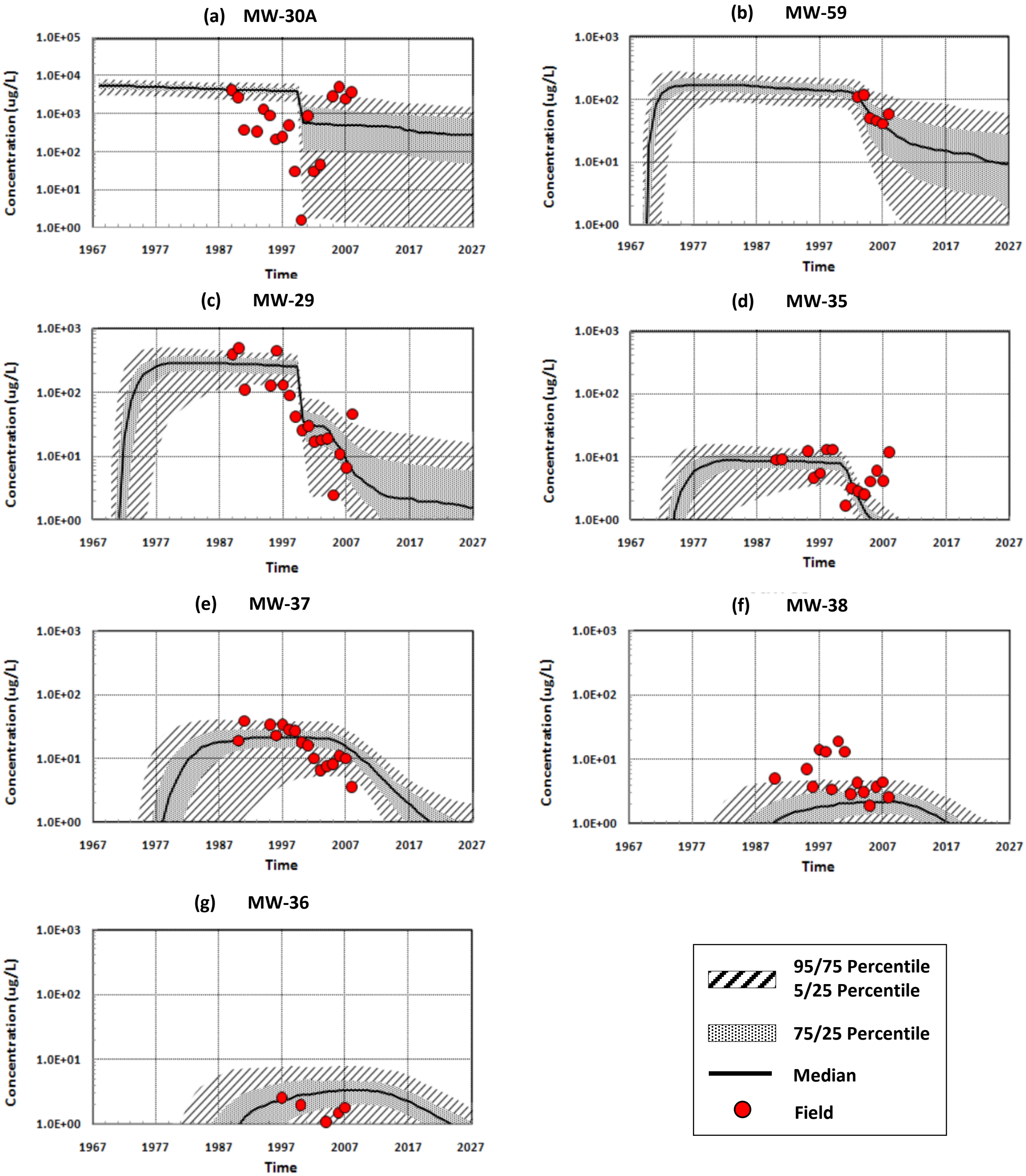

Figure 10. TCE concentrations from probabilistic simulation.

5.3 SUMMARY OF PERFORMANCE ASSESSMENT

In this project, a new probabilistic remediation model, PREMChlor, has been developed. This is achieved through linking the analytical model REMChlor to a Monte Carlo modeling simulation package GoldSim via a FORTRAN DLL application. PREMChlor can simultaneously evaluate the effectiveness of source and plume remediation considering uncertainties in all major parameters. In PREMChlor, all of the key input parameters, including source parameters, transport parameters, and remediation parameters, are treated as uncertain parameters represented by PDFs. The outputs from the PREMChlor model, including contaminant mass concentration, contaminant mass discharge, cancer risk posed by a contaminant over time at a specific location, and remediation costs, are also probability distributions and probability statistics. Such results are much more useful to decision makers who utilize the simulation results. In the PREMChlor model, a GUI has been built to allow other users to easily enter the input values, run the model, and view the results. A license-free GoldSim player file containing the GUI has been generated to make the PREMChlor model available to potential users who are not familiar with details of the probabilistic model and the GoldSim simulation environment.

This probabilistic simulation model has been applied to a TCE plume in a shallow aquifer at a manufacturing plant. Given a good understanding of the field hydrogeology and biogeochemistry, the calibrated model with a relatively simple flow field is able to closely match the pre-remediation site condition in terms of time series of TCE concentration for a large area of the contaminated site and a relatively long period of time. Probabilistic simulations predict the effects of remediation and capture most uncertainties in key parameters based on estimated PDFs.

As shown in the Final Report, the PREMChlor model has also been used to conduct sensitivity analyses by assessing the influence or relative importance of each input parameter on plume behavior, in terms of contaminant mass concentration, for three plume types. It is found that the degree of influence of different input parameters on the contaminant mass concentration varies widely for different plume types. For a stable plume that is connected to the source and a growing plume that is disconnected from the source, the parent compound concentration or the total concentration in the downgradient plume is primarily sensitive to the initial source concentration, the power function exponent, the plume degradation rate, and the chemical travel velocity, which is determined by groundwater Darcy velocity, porosity, and retardation factor. For a growing plume that is connected to the source, the concentration of a daughter compound, vinyl chloride (VC), is greatly affected by its degradation rate, the degradation rate of its direct parent cis-1,2-dichloroethylene (DCE), and transport parameters. The power function exponent affects the VC concentration greatly, and source removal fraction plays a more important role than several other parameters.

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6.0 IMPLEMENTATION ISSUES

The PREMChlor model is freely available, and it includes a comprehensive user's guide and a GUI. It is recommended that new users first familiarize themselves with the EPA REMChlor model before using PREMChlor. For users who are already familiar with REMChlor, it should be possible to have PREMChlor up and running in an hour or two.

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7.0 COST ANALYSIS

The PREMChlor model was designed to be used without extensive training in computer modeling. The underlying deterministic model, REMChlor, was released by USEPA in late 2008. Since then, REMChlor has been downloaded nearly 2000 times, and we have been involved in three one- or two-day short courses where we teach consultants, regulators, and scientists how to use the model.

It has been our experience that it takes about 8 to 16 hours of instruction and training for a groundwater or remediation professional to become proficient with the REMChlor program. This can be done through available short courses, or it may be done as a self-study, using the comprehensive REMChlor User's Guide, which contains eight tutorial examples.

Once the user is comfortable with the REMChlor program, it probably takes an additional 8 hours to become proficient with PREMChlor. Because the fundamentals of this model are the same as REMChlor, learning PREMChlor lends itself to self-study, using the PREMChlor User's Guide. This user's guide contains a complete technical description of the model, descriptions of all input variables, and four detailed tutorial examples. Our experience with the test user group (Appendix B of the Final Report) is consistent with our estimate of the time it takes to learn the PREMChlor program.

Because PREMChlor is analytically based, it is considerably easier and faster to use than full numerical models, particularly if those models are run in probabilistic Monte Carlo simulations. Probabilistic numerical model analyses require much more training (probably five to ten times more) before a user is competent at their use. Individual model set-up time for a probabilistic numerical model would also be much longer than for PREMChlor. However, in fairness, we should point out that PREMChlor is limited to problems involving relatively simple flow fields that do not change in time. There are sites where it would be more appropriate to apply a probabilistic approach with a full numerical model, despite the much higher costs involved.

One benefit of using PREMChlor instead of a deterministic approach is that remediation designs can be made more robust, that is, they can be designed so that they will still work even if some of the site parameters are different from initial estimates. While it is difficult to quantify the economic benefit of increased robustness, remediation efforts are expensive. Reducing the likelihood of remediation system failure should have a strong economic benefit.

PREMChlor was designed to be used to help optimize remediation designs. The basic procedure follows three steps: 1) initial deterministic model calibration to site data; 2) probabilistic simulation of several remediation alternatives (including cost functions); and 3) comparison of costs of remediation alternatives that meet the site constraints. This probabilistic cost optimization process is illustrated by a detailed example in the Final Report.

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APPENDIX A

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