ESTCP

EXECUTIVE SUMMARY

Evaluating and Applying Site-Specific NAPL Dissolution Rates During Remediation

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ESTCP Project ER19-5223

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Project: ER19-5223

TABLE OF CONTENTS

Page

LIST OF FIGURES

Page

ACRONYMS AND ABBREVIATIONS

DNAPL	dense nonaqueous phase liquid
DoD	Department of Defense
DPT	direct-push technology
EPA	US Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
ISCO	in situ chemical oxidation
MNA	monitored natural attenuation
NAPL	nonaqueous phase liquid
NSB	Naval Submarine Base
SCARPÉ	Source Control and Remedial Performance Evaluation

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1.0 INTRODUCTION

Remediation of nonaqueous phase liquid (NAPL)-impacted sites is difficult and costly. Even with enhancements (e.g., thermal, chemical), mass transfer constraints of NAPL dissolution govern control of sources and the attainment of cleanup goals. To better manage expenditures, the Department of Defense (DoD) needs a scientifically-based, process-centric method to evaluate the extent of control provided by past NAPL remediation and the potential benefit of additional treatment. Current approaches to predict the impact of NAPL remediation include: (1) screening models, which lack a physical basis and are simplistic, and (2) numerical transport models, which are complex and costly. The objective of this project was to establish a practical and cost-effective method to assess source control at NAPL sites by applying a volume-averaged model with a physical basis using site- and technology-specific NAPL dissolution rates.

2.0 OBJECTIVES

Performance objectives for this project included quantitative tasks to validate the source control modeling with experimental and controlled field study data, to evaluate past remedial performance at a Navy base through cleanup, and to provide support for upcoming remedial decisions at a former Air Force base. Qualitative performance objectives were ease of use and utility for supporting remedial decisions. To achieve these objectives, published mass transfer coefficients describing NAPL dissolution specific to remedial technologies and post-remediation source depletion were compiled and incorporated within a volume-averaged model that includes coupled processes. The overall technology is referred to as Source Control and Remedial Performance Evaluation (SCARPÉ). The approach minimizes spatial specificity, limits the required site-specific inputs, and reduces the burden of parameter estimation and calibration. The method is based on mass balance principles with a physical basis and is adaptable to available data and varied processes. This approach was validated experimental data and numerical transport modeling and demonstrated at two sites with various NAPL architectures exposed to multiple remedial processes. The effort resulted in beta versions of two practical tools (SCARPÉm and SCARPÉs for multi- and single-component NAPL, respectively). The calculation tools were provided to remedial project managers, regulators, consultants and other stakeholders for feedback on the ease of use and utility of the output for remedial decisions.

3.0 TECHNOLOGY DESCRIPTION

A straightforward, upscaled NAPL mass dissolution model was developed with relatively simple input consisting of characteristic dimensions and saturations of a NAPL accumulation. Multiple accumulations were aggregated into a single source zone volume. An example source zone conceptualization is illustrated in Figure ES-1. Physically, the dissolution process is a combination of flow through the mass (advective component) and flow around the mass (dispersive component). The contribution of each component is based on initial characteristic length scales and saturations. Changes over time with the depletion of mass are captured with a changing relative permeability and a power law relationship for the fraction of initial mass remaining. Including the contributions from local dispersion in the dissolution model is a significant and useful departure from convention. The model output provides a temporal history of the mass discharge rate and the average discharge concentration.

The input parameters are minimal and are found in typical NAPL source zone characterization data or can be interpreted indirectly through evaluation of the downgradient plume.

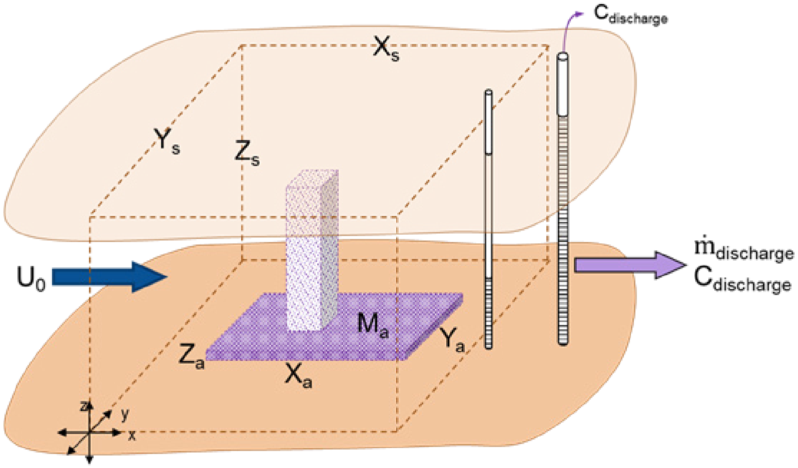

Figure ES-1. Conceptualization of a Model Source Zone and NAPL Architecture

The larger source zone volume, V_s, encompasses multiple ganglia-, pool-, or mixed-type NAPL accumulations encompassing all the NAPL masses. Multiple NAPL accumulations of relatively uniform saturation make up the NAPL architecture, each with characteristic dimensions, which can represent ganglia-, pool- or mixed-type NAPL accumulations. With dimensional variables defined in Figure ES-1, the governing equations for NAPL mass, M, with solubility C^* and resulting discharge concentration, C, are,

$$\frac{1}{V_s}\frac{dM_n}{dt} = -K_n(C^* - C) = -\sum_{a=1}^{A} K_a\left(C^* - C_{a,0}\right) \quad \textbf{(E-1)}$$

$$R\frac{dC}{dt} = -\frac{U_0}{\phi X_s}\mathrm{C} - \frac{1}{\phi V_s}\frac{dM_n}{dt} - r(t) \quad \textbf{(E-2)}$$

The NAPL mass transfer coefficient based on engineering process models (Stewart et al. 2022) is,

$$K_{a,0}(m_a) = \frac{U_0}{V_s}\left[A_{a,yz}\, k_r(m_a) + A_{a,xy}\sqrt{\frac{4\alpha_T}{\pi X_{a,0}}}\right]\left(\frac{m_a}{m_{a,0}}\right)^{\gamma} \quad \textbf{(E-3)}$$

This expression for $K_{a,0}$ is solely a function of the mass within the dense nonaqueous phase liquid (DNAPL) sub-volume given the upscaled velocity (U_0), characteristic projected area to flow (A_{yz}), a relative permeability function (k_r), tangential area for dispersion (A_{xy}) with dispersivity α_T, and a single exponent γ. The exponent value is expected to a range from 0.5 to 0.67 based on theoretical evaluations of pool and ganglia architecture, respectively. Simple approximate solutions were derived by assuming an average, constant relative permeability which in turn provides reasonable estimates for the time required for NAPL depletion.

Estimates for remediation are captured through a transient reactive term, r, which can be linked to other mass balances for remedy amendments. In addition, theoretical and empirical correlations are available from the literature to estimate remedy-specific dissolution enhancements,

$$K_n = K_{n,0} E_r E_f \,, \qquad U = U_0 E_f \,, \qquad E_r = f(r)\,, \qquad C^* = C_0^* E_s \tag{E-4}$$

The factor E_f represents changes in the characteristic velocity through the NAPL soil volume, e.g., pump-and-treat. E_r is a reactive enhancement on mass dissolution resulting from the addition of amendments, e.g., chemical oxidants, and is a function of these reactions. E_s is an estimated multiplier for the effective solubility in presence of a solubilizing agent, e.g., cosolvents. Theoretical and empirical approaches to estimate these enhancements are available in the literature and were demonstrated in this work.

4.0 PERFORMANCE ASSESSMENT

The first quantitative performance objective entailed validating and demonstrating the set of governing equations for the dissolution of distributed NAPL masses and the resulting discharge concentration and mass discharge rates from the NAPL-impacted soil volume. This was achieved by matching experimental data. Examples of the results are depicted in Figure ES-2 for a dissolution experiment with mixed DNAPL architecture and partial destruction of a DNAPL pool in an experiment with in situ chemical oxidation (ISCO). The matching was successful.

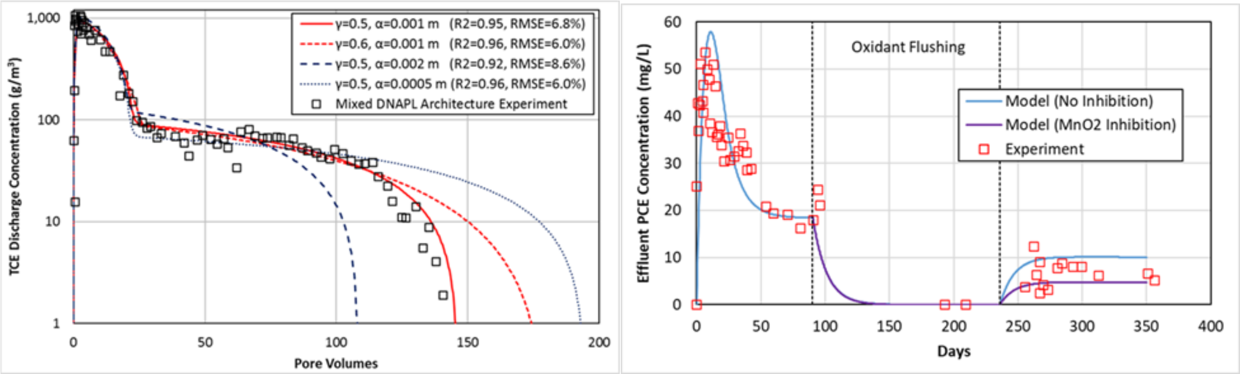

Figure ES-2. Model Applications to Dissolution and Remediation Experiments

In a second quantitative performance objective, the modeling approach was demonstrated at a well-documented DNAPL site in a moderately complex setting. At Site 11 Naval Submarine Base (NSB) Kings Bay, the model successfully provided a robust interpretation for the full life cycle of a DNAPL source zone as depicted in Figure ES-3. The interpretation was based on matching trends observed during and after site activities, including natural dissolution, groundwater extraction, mass destruction through ISCO, and a long tailing associated with back diffusion. The evaluation of remedial alternatives confirmed that monitored natural attenuation (MNA) alone was unacceptable, multiple intensive applications of ISCO were highly successful, and pump-and-treat may have provided a cost competitive approach for attaining drinking water standards.

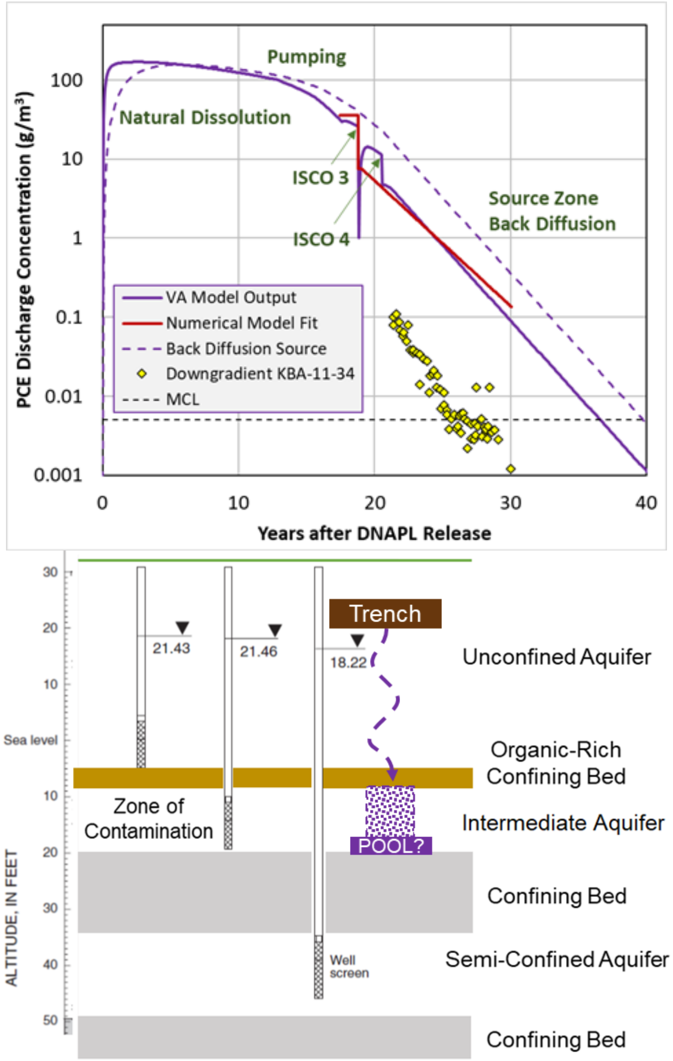

Figure ES-3. Volume-Averaged Model Interpretation of a DNAPL Source Zone Life Cycle

The third quantitative performance objective evaluated the model for supporting remedial decisions at a very complex site, ST012 at the Former Williams Air Force Base, which was impacted by millions of gallons of kerosene-type jet fuel spread over about 10 acres. This complex site included multiple, NAPL-impacted water-bearing units and a water table rise of 90 feet over the past 30 years. Remedial history included limited pump-and-treat, MNA studies, thermal treatment, and on-going enhanced bioremediation.

A recent full-scale application of steam enhanced extraction removed roughly 400,000 equivalent gallons of NAPL and fuel components from the site leaving approximately 200,000 gallons of untreated NAPL in surrounding areas. Detailed geologic logs with field NAPL test kits were collected from over 40 soil borings and presented a NAPL architecture of discrete pools vertically dispersed under fine-grained material. The ST012 evaluation of remedial alternatives considered MNA, enhanced bioremediation, pump-and-treat, and ISCO with technology-specific dissolution enhancements. Example output for one target treatment zone alongside the geologic and NAPL detection data used for characterization are illustrated in Figure ES-4.

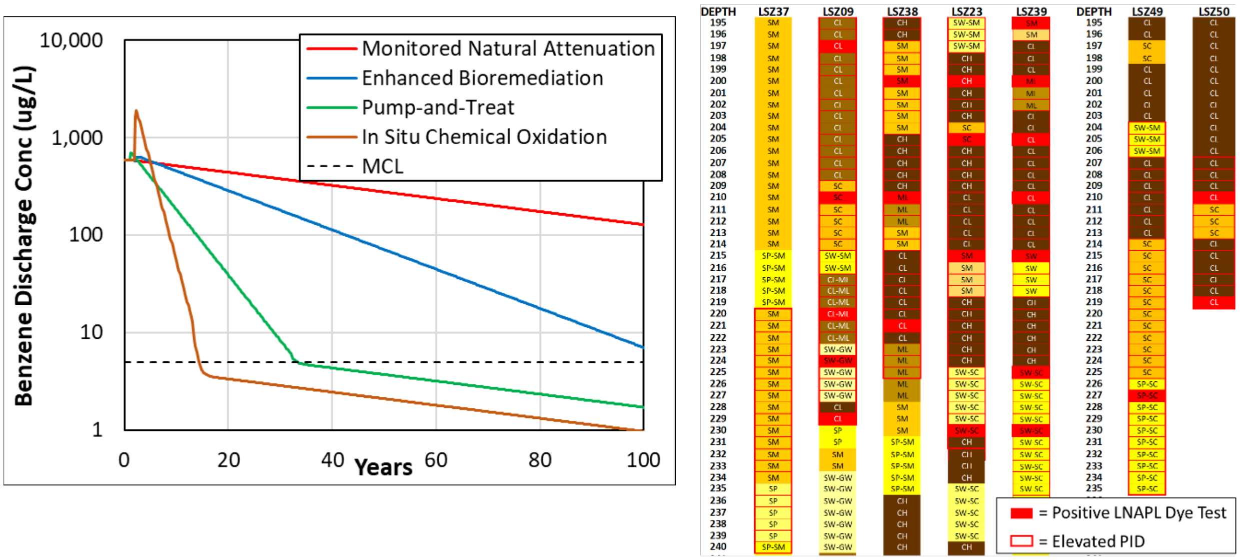

Figure ES-4. Model Comparison of Remedial Alternatives at a Complex Site

Qualitative performance objectives for the project were ease of use and utility for supporting remedial decisions. The objectives were met based on feedback obtained through direct contact with remedial project managers, regulators, consultants and other stakeholders. Users were provided with beta version tools and all were able to run these simple tools for template scenarios and assess the outputs without extensive training. The utility of the model results for remedial decisions was confirmed by remedial project managers; however, users cited the main implementation and utility issue as development of the conceptual source model and identification of input parameters (i.e., how to get the information).

5.0 COST ASSESSMENT

Implementation of the SCARPÉ tools relies on three cost elements: (1) data compilation and assimilation, (2) volume-averaged modeling (using a computer), and (3) analysis and reporting of results. The SCARPÉ mathematical framework and the two practical tools are provided free of charge. In addition, the data necessary to develop the conceptual source zone model and determine the input parameters are expected to be available at sites undergoing investigations and remediation. Therefore, the main cost driver for implementation of the NAPL dissolution tool is the labor cost (i.e., time). The cost to implement two SCARPÉ tools is estimated to be on the order of $23,000. This cost is a fraction of the cost to develop and use complex numerical models for NAPL dissolution and is consistent with the costs for application of screening-level models. However, in contrast to screening-level models, the volume-averaged approach is physically-based, and provides better prediction and scientifically defensible comparisons between remedial alternatives. Application of the volume-averaged approach is also expected to provide cost-savings at DoD sites, by supporting the selection of the most efficacious remedy to achieve cleanup goals.

6.0 IMPLEMENTATION ISSUES

Based on user feedback, additional guidance was provided on estimating input parameters for the modeling. Site investigations and associated investigation reports at NAPL sites would typically include data needed to develop the conceptual source zone model as illustrated in Figure ES-5. Therefore, access to historical investigation and remediation information and involvement of practitioners familiar with the site and its history would facilitate application of the technology. The demonstrations included extensive descriptions of methodologies for interpreting downgradient plume histories and high-resolution measurements to characterize the source zone. Sites with existing transport models can leverage the transport model for data interpretation.

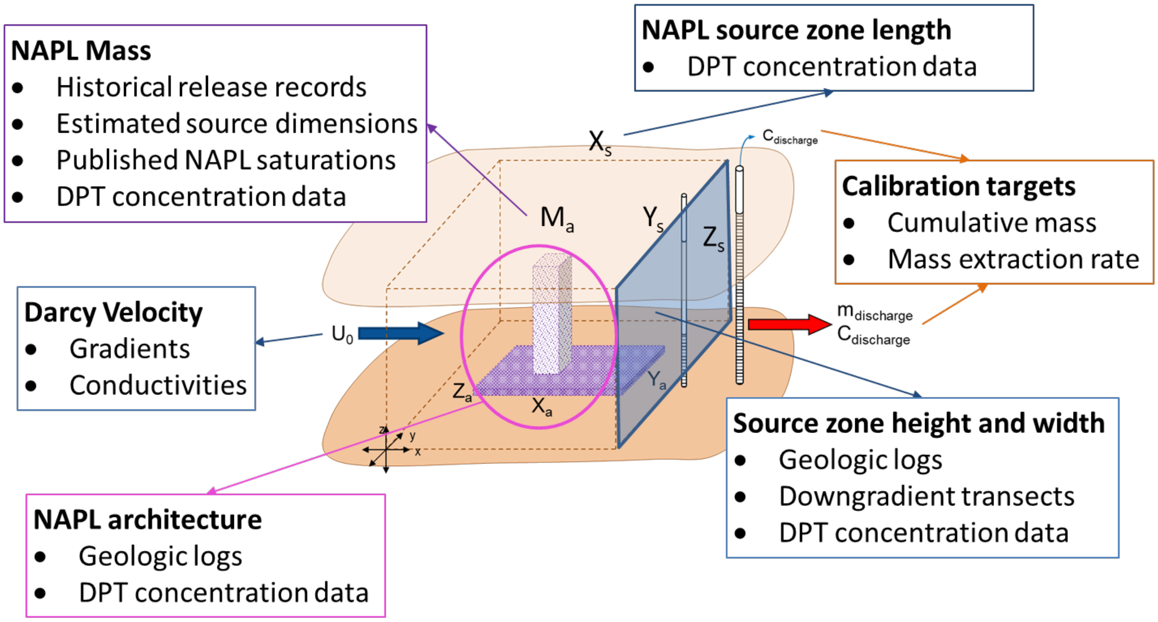

Figure ES-5. Example Sources of Data and Interpretation for Estimating Input Parameters

More complex implementations of the modeling approach can readily be implemented and solved using available coding platforms such as Matlab or FORTRAN, however, it does require coding and specialty users. As part of this work, two practical ready-to-use tools, which do not require any specific training, or software and can be run on a personal laptop. When limited information is available to develop a conceptual source model, sensitivity and uncertainty analysis methods can be readily coupled with the model framework to identify controlling parameters and prioritize data collection to refine the conceptual source model.

7.0 REFERENCES

Stewart, L.D., Chambon, J.C., Widdowson, M.A., Kavanaugh, M.C. 2022. Volume-averaged modeling of complex DNAPL dissolution. Journal of Contaminant Hydrology 244, 103920.