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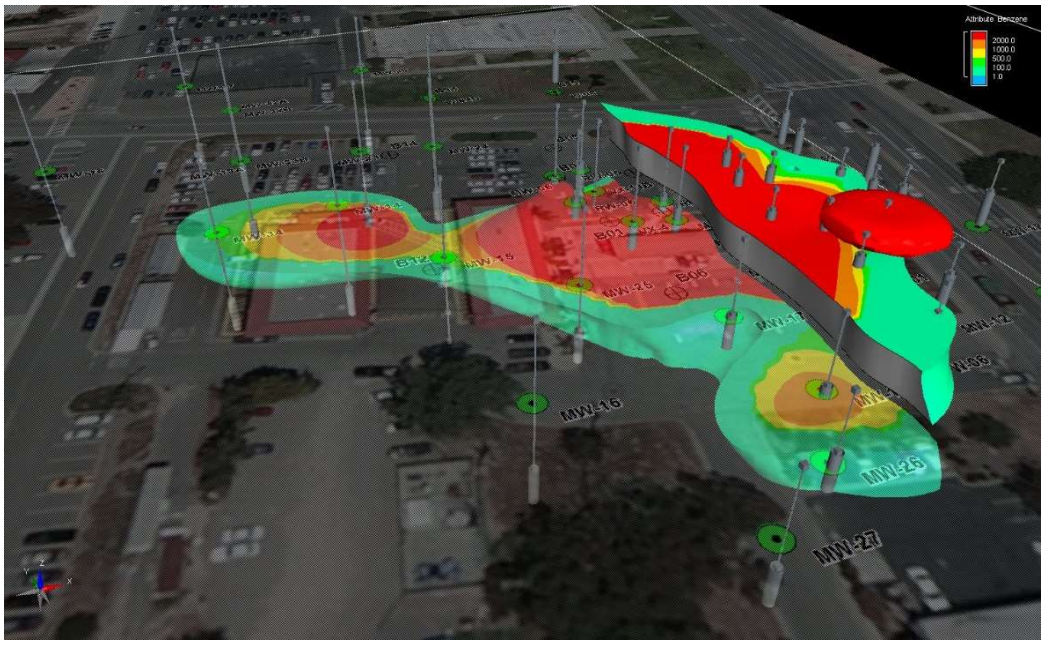
TOOLS FOR ESTIMATING CONTAMINANT MASS-IN-PLACE, MASS DISCHARGE, AND REMEDIATION TIMEFRAMES



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The development of a quantitative estimate of the contaminant mass present in a target treatment zone offers important benefits to project stakeholders including improving the accuracy of projected remediation costs and timeframes. Tracking changes in contaminant mass and/or mass discharge over time can also provide important metrics for assessing remediation progress. This document provides an overview of tools and techniques to estimate contaminant mass-in-place, contaminant mass discharge, and remediation timeframes. Tools applicable to each type of calculation are reviewed followed by a case study that illustrates how tool results were used to improve site-specific remedial strategies.

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EXECUTIVE SUMMARY

The development of a quantitative estimate of the contaminant mass present in a target treatment zone offers important benefits to project stakeholders. These benefits include understanding the magnitude of contaminant impact and improving the accuracy of projected remediation costs and timeframes. Tracking changes in contaminant mass and/or mass discharge over time can also provide important metrics for assessing remediation progress. This document provides an overview of tools and techniques to estimate contaminant mass-in-place, contaminant mass discharge, and remediation timeframes. These tools, summarized in Table ES-1 below, range from back-of-the-envelope calculations to more sophisticated three-dimensional (3-D) modeling and are meant to assist Remedial Project Managers (RPMs) in developing an improved conceptual site model (CSM) based on quantitative analysis of the site data. Typically, tools that involve greater data input and computation can yield more accurate mass estimates. However, an order-of-magnitude estimate of contaminant mass can be effectively used to screen remedies and explore various remedial optimization strategies.

Table ES-1. Summary of Methods and Models Reviewed in this Document

Tool	Applicability		Contaminant Mass-in-Place	Contaminant Mass Discharge	Remediation Timeframe
	Source	Plume			
Isoconcentration Contour Method	X	X	X	X	
Matrix Diffusion Toolkit	X	X	X	X	X
Mass Flux Toolkit		X		X	
3-D Numerical Solute Transport Models	X	X		X	X
3-D Interpolation	X	X	X		
SourceDK	X		X		X
BIOCHLOR & BIOSCREEN		X			X
Natural Attenuation Software	X	X			X
REMChlor/REMFuel		X			X

This document reviews key considerations when selecting and applying these quantitative tools to support improved site management and remediation decisions. The document is comprised of three main sections: Mass-in-Place (Section 2.0), Mass Discharge (Section 3.0), and Remediation Timeframes (Section 4.0). Tools applicable to each type of calculation are reviewed followed by a case study that illustrates how tool results were used to improve site-specific remedial strategies. A resource section provides links to additional information and the necessary software (where applicable).

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ACRONYMS AND ABBREVIATIONS

3-D	three-dimensional
AFCEE	Air Force Center for Engineering and Environment
cm^3	cubic centimeter
COC	contaminant of concern
CSM	conceptual site model
d	day
DCE	dichloroethylene
DoD	Department of Defense
DOS	distance of plume stabilization
ESTCP	Environmental Security Technology Certification Program
foc	fraction of organic carbon
ft	foot
g	gram
gal	gallon
IC	institutional control
IR	Installation Restoration
ISCO	in situ chemical oxidation
ITRC	Interstate Technology Regulatory Council
Koc	octanol-water partitioning coefficient
lb/yr	pound/year
m	meter
m^2	square meter
MNA	monitored natural attenuation
NAPL	non-aqueous phase liquid
NAS	Natural Attenuation Software
SADA	Spatial Analysis and Decision Assistance
TCE	trichloroethylene
TOD	time of NAPL dissolution
TOR	time of remediation
TOS	time of stabilization

US EPA	United States Environmental Protection Agency
VC	vinyl chloride

1.0 INTRODUCTION

The development of a quantitative estimate of the contaminant mass present in a target treatment zone offers important benefits to project stakeholders. These benefits include understanding the magnitude of contaminant impact and improving the accuracy of projected remediation costs and timeframes. Tracking changes in contaminant mass and/or mass discharge over time can also provide important metrics for assessing remediation progress. Despite these benefits, practitioners may sometimes choose not to develop quantitative mass estimates due to perceptions about the complexity of the calculations and/or concerns about the uncertainty of the results. Fortunately, a variety of mass estimation tools can be effectively used to estimate contaminant mass-in-place, contaminant mass discharge, and remediation timeframes. This document provides an overview of tools and techniques for evaluating these important site restoration metrics. Several of the tools have been developed and validated under Department of Defense (DoD) or other Federal Government programs.

The tools presented herein range from back-of-the-envelope calculations to more sophisticated three-dimensional (3-D) modeling. These tools can vary in terms of data input requirements, complexity, computational requirements, and accuracy. Typically, the tools that involve a greater degree of data input and computation can yield more accurate mass estimates; however, for some projects, a simple calculation of contaminant mass may provide important value to the remediation program. Mass estimates are important outcomes of a site investigation and are fundamental to the conceptual site model (CSM) for understanding the contaminant hydrogeologic system at a given site. This document reviews key considerations when selecting and applying these quantitative tools to improve CSMs and support site management and remediation decisions.

2.0 MASS-IN-PLACE

Contaminant mass includes the amount of the contaminant of concern (COC) present in the subsurface in the source zone and the dissolved-phase groundwater plume. The source zone is defined as the portion of the site that contains free-phase non-aqueous phase liquid (NAPL), residual NAPL, and/or contaminant mass adsorbed to the geologic matrix. Contaminant mass may be present in the vadose and/or saturated zones. However, in this document, only mass contributions in the saturated zone are considered. Additional calculations and modeling approaches are required if substantial mass is anticipated to be present in the vadose zone.

The contaminant mass is defined as the amount of COC that is contained in the following three compartments:

- free-phase or residual NAPL mass;
- mass adsorbed to the geologic matrix; and
- mass dissolved in groundwater.

In the source zone, the dissolved mass is often negligible compared to the sorbed mass (GSI,

2011). Mass estimation approaches for these three compartments are described in Table 1.

Table 1. Contaminant Mass Calculations

$Residual\ mass = S_R \cdot \theta \cdot V_R \cdot \rho$
S_R – Residual saturation (unitless). It is the volume of residual NAPL present in a unit volume of pore space. It typically varies between 5% and 30% of pore space in both porous and fractured media (Kueper and Davies, 2009). θ – Aquifer porosity (unitless). It is the ratio of the volume of voids to the bulk volume of the aquifer matrix V_R – Volume of the aquifer (L^3) where residual NAPL is present ρ – NAPL density (M/L^3)
$Sorbed\ mass = C_S \cdot M_S = C_S \cdot V \cdot \rho_b$
M_S – Mass of contaminated soil (M), which is equal to the volume of aquifer (V) where contamination is present (L^3) multiplied by the dry bulk density of the soil (ρ_b) (M/L^3) C_S – Average soil concentration (M/M). The soil concentration can be estimated based on the aqueous concentration (C_W) (M/L^3) as follows: $C_S = C_W \cdot K_d = C_W \cdot K_{OC} \cdot f_{OC}$ C_W – Average aqueous concentration (M/L^3) K_d – Partition (or distribution) coefficient (L^3/M) K_{OC} – Organic carbon-water partition coefficient (L^3/M) f_{OC} – Fraction organic carbon on uncontaminated soil (unitless)
$Dissolved\ mass = C_W \cdot V_w = C_W \cdot V \cdot \theta$
C_W – Average aqueous concentration (M/L^3) V_W – Volume of water where contamination is present (L^3) θ – Aquifer porosity (unitless) V – Volume of aquifer (L^3) where dissolved-phase contamination is present

2.1 TOOLS FOR MASS ESTIMATION

The tools described in this document are presented in order of increasing complexity of the data requirements and estimation process. The order presented also provides a contaminant mass estimate with an increasing level of certainty and confidence. Table 2 summarizes mass estimation tools and their data inputs and outputs as described below.

Table 2. Summary of Mass Estimation Tools

Tool	Scale		Data Inputs	Data Outputs	Pros	Cons	Additional Comments
	Source	Plume					
Isoconcentration Contour Method	X	X	• Concentration at monitoring wells • Isoconcentration contour map • Aquifer thickness, porosity • Distribution coefficient and soil bulk density (mass calculation) • Hydraulic conductivity and gradient (mass discharge calculation)	• Dissolved and sorbed contaminant mass • Mass discharge at select transects	• Relies on existing isoconcentration contour maps • Minimum data requirement • Easy and fast to implement • Estimate can be part of routine monitoring reports • Applicable to both source and plume scales	• Assumption of uniform properties • Low permeability zones are not taken into account	
SourceDK	X		Mass Estimate • Method 1: Average soil concentration, volume of source zone, and soil bulk density • Method 2: Extent of NAPL zone, soil bulk density, measured soil concentrations in NAPL zone, porosity, measured dissolved concentrations, distribution coefficient and soil bulk density • Method 3: NAPL saturation, porosity, volume of NAPL zone and density of NAPL source Remediation Timeframe • Initial concentration, desired cleanup level, source zone length, seepage velocity, retardation factor, and if NAPL constituents, type of media, density of NAPL fluid, NAPL saturation and seepage velocity under pumping conditions	• Mass versus time charts • Number of pore volumes and time required to achieve desired cleanup level	• Provides four averaging methods to compute average soil/aqueous concentrations • Excel-based • Can account for effect of pumping	• Does not account for matrix diffusion when calculating number of pore volumes required to achieve cleanup • Only applicable to the source zone	Development funded by the U.S. Air Force Center for Engineering and Environment (AFCEE)
Matrix Diffusion Toolkit	X	X	• Loading period, source concentration, time of source removal • Diffusion coefficient, tortuosity factor, porosity and sorption parameters in the low-permeability zone • Darcy velocity, hydraulic conductivity and gradient and degradation rate in the transmissive zone	• Mass discharge over time • Concentration in transmissive zone over time • Mass in transmissive zone over time • Aqueous, sorbed, and total concentrations in low-permeability zone over time (Dandy-Sale Model only)	• Takes into account matrix diffusion • Provides mass estimates in both transmissive and low-permeability zones • Includes degradation in the transmissive zone • Includes evaluation of uncertainty, with possibility to run Monte-Carlo analysis • Can be calibrated with available monitoring data • Includes consideration of DNAPL removal in the source zone	• Estimates relies significantly on the loading period and concentration during loading periods, which are difficult to estimate • Does not include degradation in the low-permeability zone, which can be an importance attenuation process • Cannot be used to estimate remediation timeframe for partial source mass removal	Development funded by DoD Environmental Security Technology Certification Program (ESTCP)
3-D Interpolation	X	X	• Concentration at monitoring wells • Porosity and sorption parameters	• Contaminated volume • Dissolved and sorbed contaminant mass	• Minimum data requirement • Estimate can be part of routine monitoring reports • Applicable to both source and plume scales	• Estimates depend on interpolation scheme	

2.1.1 Isoconcentration Contour Method

This method for estimating contaminant mass relies on the development of isoconcentration contours of the COCs. It mainly uses information generated as part of routine groundwater monitoring and reporting activities. It can be applied to estimate the contaminant mass in the source zone or the dissolved-phase groundwater plume. For the source zone, the potential for residual NAPL should be evaluated and the associated contaminant mass should be added to the contaminant mass estimate described below. This method is based on the following steps:

- Prepare isoconcentration contour maps for the COCs. If multiple aquifers (or hydro-stratigraphically separate units) are present, one map per aquifer may improve the accuracy of this method.
- Calculate the area (A_i) between adjacent isoconcentration contours.
- Estimate the average aqueous concentration ($C_{W,i}$) between isoconcentration contours. Note that different approaches exist to estimate the average aqueous concentrations such as:
  - Use the arithmetic or geometric mean of all concentrations inside the isoconcentration contour;
  - Use the arithmetic or geometric mean between two isoconcentration contours; or
  - Use kriging or interpolation software, such as Surfer® (Ricker, 2008).
- Estimate the aquifer thickness (b) and total porosity (θ).
- Determine values for the distribution coefficient (K_d) based on published K_{OC} values and measurements of the soil's fraction of organic carbon content (f_{OC})[1] and as well as the dry bulk density of the soil. This information is used to calculate the average soil concentration (sorbed mass).
- Calculate the total contaminant mass as shown in Table 3.

Table 3. Calculation of Total Contaminant Mass Using the Isocontour Method

$$\textit{Contaminant Mass} = \sum C_{W,i} \cdot A_i \cdot b \cdot (\theta + K_d \cdot \rho_b)$$
$C_{W,i}$ – Average aqueous concentration (M/L^3) in each isoconcentration contours
A_i – Area between two adjacent isoconcentration contours (L^2)
b – Aquifer thickness (L)
θ – Aquifer porosity (unitless)
K_d – Partition (or distribution) coefficient (L^3/M)
ρ_b – dry bulk density of the soil (M/L^3)

[1] If the fraction of organic carbon in soil is unknown, published literature values based on soil type may be used, but can reduce the accuracy of the result.

This method relies on the assumption that the geologic matrix is uniform within the extent of the source zone and the groundwater plume. It does not consider the significant heterogeneities that are present at most sites or low permeability zones, which might contain higher levels of sorbed contaminant mass (Chapman and Parker, 2005; GSI, 2011). Hence, the utility of this method is limited to providing an order of magnitude estimate of contaminant mass present.

2.1.2 SourceDK

The Microsoft® Excel-based software SourceDK (GSI, 2011) can be used to estimate the contaminant mass in the source zone. The software provides three different methods for calculating contaminated mass:

- The "Simple Volume x Concentration Calculation" method is based on the average soil concentration in the saturated source zone, the volume of the source zone (thickness and area) and the soil bulk density. It requires the user to compute the average soil concentration. This method might underestimate the total contaminant mass since only the contaminant concentration in soil is considered. Residual NAPL and dissolved-phase mass are not considered. The accuracy of this method is highly dependent on the technique used to estimate the concentration in soil. Analytical methods that account for sorbed and residual mass (e.g., extraction-based methods) may improve its accuracy.
- The "Detailed Volume x Concentration Calculation" method is based on actual groundwater and soil concentration data in each phase. The mass in each is estimated as follows:
  - Residual NAPL mass is calculated based on extent of the NAPL zone (area and thickness), soil bulk density, and average of measured soil concentrations in the NAPL zone;
  - Dissolved mass is calculated based on the source zone extent (equal to the NAPL zone extent if NAPL is present), porosity, and the average of measured dissolved phase concentrations;
  - Sorbed mass downgradient (e.g., outside of the area where residual NAPL is known to be present) is calculated based on the dissolved mass and sorption parameters (partition coefficient, porosity, soil bulk density); and
  - Several averaging methods are available to compute the average concentrations based on up to 30 measured values, including area-weighted average.
- The "Estimated from NAPL Relationships" method is based on NAPL saturation, aquifer porosity, the volume of the NAPL zone (area and thickness), and the density of the source NAPL. This method only accounts for the residual NAPL mass, which is a reasonable assumption in many cases, because it generally represents the majority of the contaminant mass in the source zone.

2.1.3 Matrix Diffusion Toolkit

The Microsoft® Excel-based Matrix Diffusion Toolkit can be used to estimate the contaminant mass in the transmissive (aquifer) and low-permeability (aquitard) zones for the source zone or downgradient groundwater plume (see Figure 1). The Matrix Diffusion Toolkit provides two

models to calculate the contaminant mass, both based on the conceptual model of a two-layer system and a loading period followed by a release period (GSI, 2012):

- The "Square Root Model" provides an estimate of the contaminant mass in the low-permeability zone over time. The model considers the loading period, which is defined as the period during which the concentrations in the more permeable zone were greater than those in the low permeability zone (GSI, 2012). The model also considers the contaminant concentration during the loading period, the transport characteristics of the low-permeability zone (diffusion coefficient, tortuosity factor, porosity, and sorption parameters), and the area of interest (source zone or downgradient plume). The transport properties for the transmissive zone (Darcy velocity, hydraulic conductivity, and gradient) are also required. These parameters are used to estimate the concentration in downgradient monitoring wells that can be compared and calibrated with site-specific data.
- The "Dandy-Sale Model" is more sophisticated than the "Square Root Model" and requires additional input data. This model provides an estimate of the contaminant mass both in the transmissive and low-permeability zones over time. Similar to the Square Root Model, it considers the loading period, the source concentration during the loading period, the transport characteristics of the low-permeability zone, and the source area. In addition, it considers the transport properties of the transmissive zone including Darcy velocity, hydraulic conductivity, hydraulic gradient, and sorption parameters.

The main parameters in the Matrix Diffusion Toolkit are the loading period and the contaminant concentration during the loading period. Those parameters are difficult to estimate at most sites due to the absence or limitations of historical monitoring data and information. However, the matrix diffusion models can be calibrated to available monitoring data, which can help to constrain the data inputs. By default, a lower range, consisting of a most likely value and an upper range are provided for the contaminant mass. The software incorporates a Monte Carlo-type approach to quantify uncertainty.

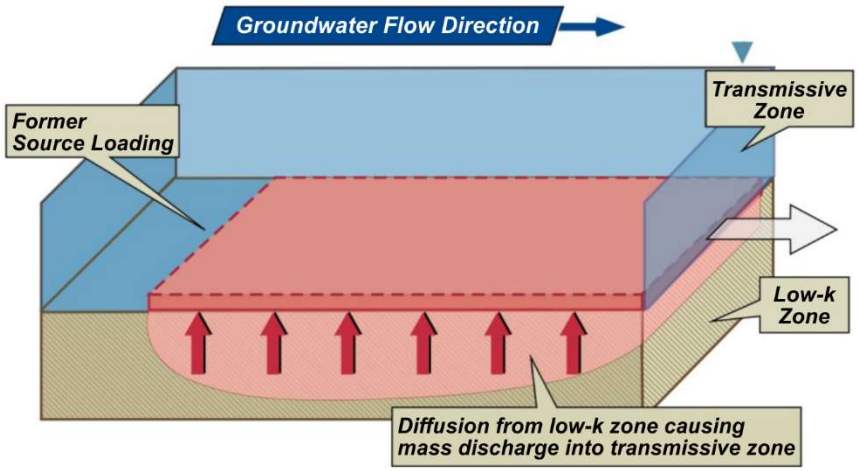

Figure 1. Matrix Diffusion Illustration (Courtesy of GSI, 2012)

2.1.4 Three-Dimensional Interpolation Using Geographic Information Systems

3-D interpolation software, such as Earth Volumetric Studio® or the free software Spatial Analysis and Decision Assistance (SADA) (Stewart et al., 2009), can be used to estimate contaminant mass-in-place. Required data include contaminant concentrations, porosity, and sorption parameters. Concentrations can be gathered and interpolated from monitoring data (see Figure 2). Porosity and sorption parameters can be acquired by collecting and testing soil cores, or alternatively, estimated from the literature using available site-specific lithologic and geochemical information.

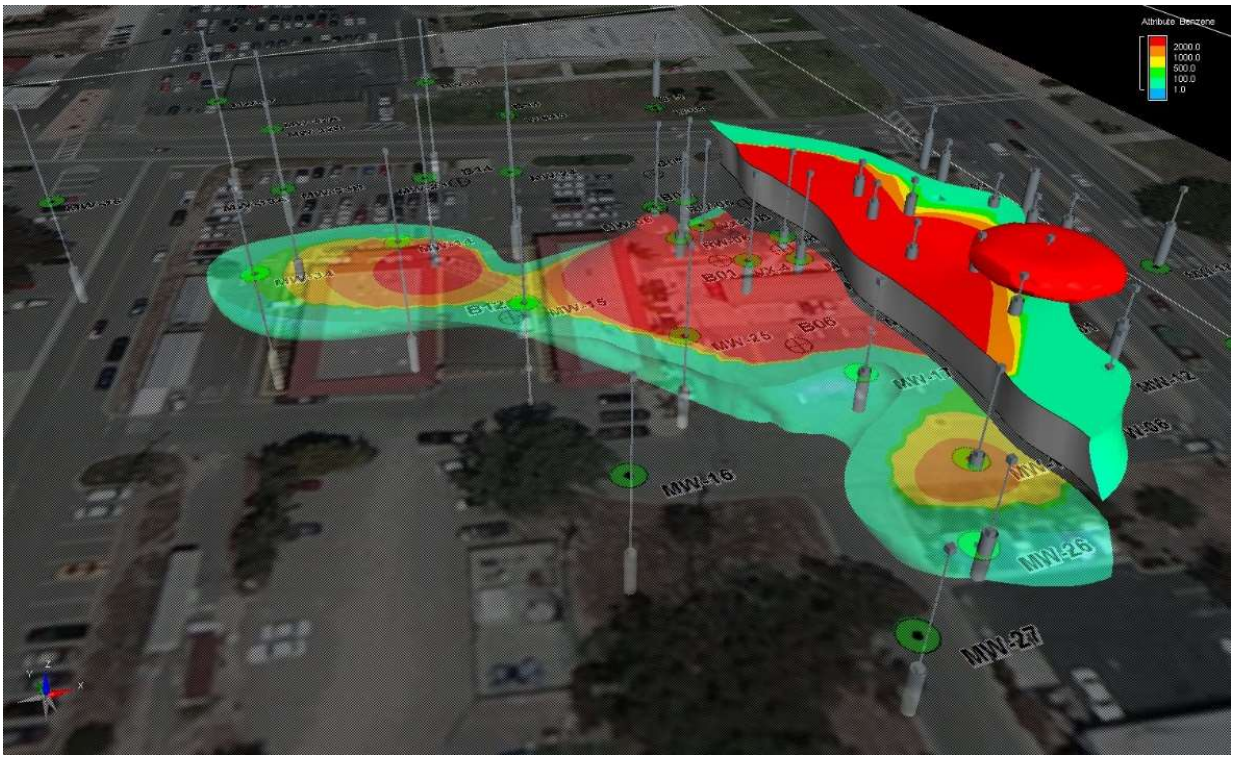

Figure 2. Example of 3-D Interpolation of a Benzene Plume (Courtesy of Battelle)

2.2 MASS ESTIMATE CASE STUDY: FORMER NAVAL AIR STATION ALAMEDA

Maintenance activities at Installation Restoration (IR) Site 26, located at the former Naval Air Station Alameda, California resulted in the release of trichloroethylene (TCE) into the environment. Groundwater was found to be impacted with TCE, as well as its daughter products dichloroethylene (DCE) and vinyl chloride (VC). To address these contaminants, a remedy was implemented consisting of in situ chemical oxidation (ISCO) followed by enhanced in situ bioremediation (EISB).

The isoconcentration contour method (Table 4) was used to estimate the mass of chlorinated ethenes at the site before and after a pilot-scale ISCO application with activated hydrogen peroxide. This method was selected as a quick and inexpensive way to determine a rough order of magnitude for contaminant mass in the target treatment zone. The mass estimate helped to evaluate the amount of oxidant required for each target treatment interval and provided one line of evidence for treatment efficiency after each ISCO injection event. As shown in Figure 3, groundwater

concentration data were collected from monitoring wells eight weeks after performing the pilot test and used to generate a series of contours for the three COCs. A kriging approach was applied, which is a statistical gridding method to spatially interpolate concentrations based on values and distances between adjacent sampling locations. This approach provided for an estimate that spatially weighted the mass generated from each monitoring location using the area between contours and an estimated average concentration (C_w). To be conservative, the average detected concentration for each of the three COCs, excluding all non-detect results, was used to calculate the mass of contamination in groundwater.

Table 4. Total VOC Mass Estimates for IR Site 26, Former Naval Air Station Alameda

VOC	Volume (ft^3)	VOC Mass in Aqueous Phase (lb)	Soil Sorption Coefficient K_{oc}	Organic Carbon Fraction in Soil f_{oc} (%)	Distribution Coefficient K_d (ft^3/lb)	VOC Mass on Soil (lb)	Total Mass in Target Area (lb)
VC	32,780	0.0101	2.45	0.25	0.00016	0.0004	0.01
DCE	16,984	0.0653	49	0.25	0.0019	0.047	0.11
TCE	29,293	0.0185	126	0.25	0.0051	0.034	0.05

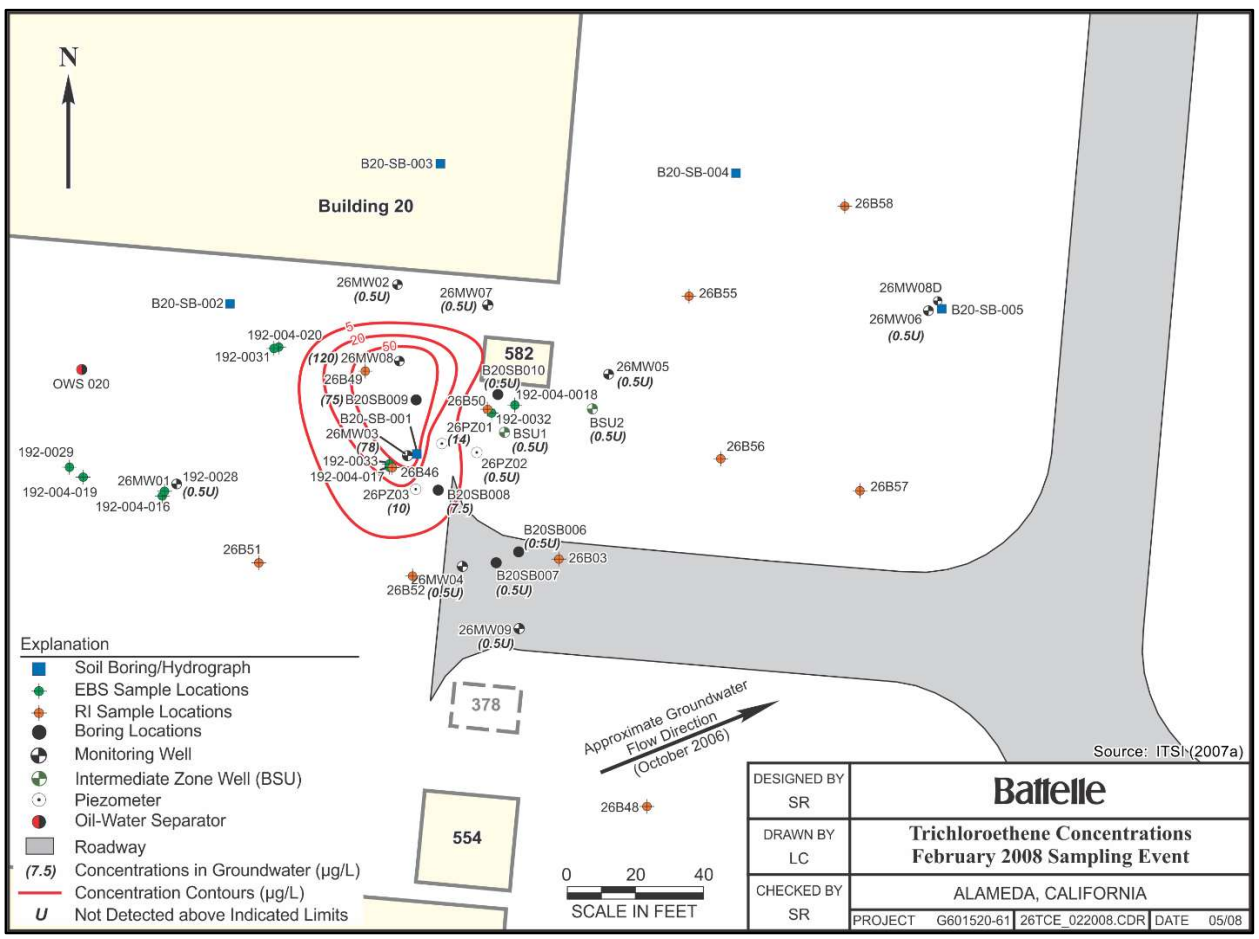

Figure 3. TCE Isoconcentration Contours Generated for IR Site 26, Former Naval Air Station Alameda (Courtesy of Battelle)

The estimated total volume of contaminated aquifer media was based on the areal extent (A) of TCE, DCE, and VC exceeding their remedial goal concentrations in groundwater of 5, 6, and 0.05 µg/L, respectively. An 11-ft-thick vertical interval (b) of contamination was assumed to calculate the volume of contaminated media.

The value for porosity (θ), 30%, was selected based on known site lithology and the results of an aquifer pump test. Dry bulk density values (ρ_β) were determined using data collected during previous investigations, having an average value of 1.7 g/cm^3.

The K_d was determined for each COC using published Koc values and the foc measured in soil samples. Organic carbon values, ranging from 0.2 to 0.36 (average of 0.25), were determined during results of previous investigations.

The total mass of each COC was estimated using the isoconcentration contour method equations and the data described above. Results were then compared to similar calculations of mass remaining after each ISCO injection event and helped to determine the amount of oxidant to apply each time.

3.0 MASS DISCHARGE

Mass flux is the mass of a COC that passes through a defined cross-sectional area per unit time, perpendicular to the direction of groundwater flow. It is expressed as mass/time/area (i.e., g/day/m^2). Mass discharge is related to mass flux, but it represents the total mass of a COC moving in the groundwater from a given source, and is expressed as mass/time (e.g., g/day). These concepts are graphically illustrated in Figure 4 and are defined by the equations presented in Table 5.

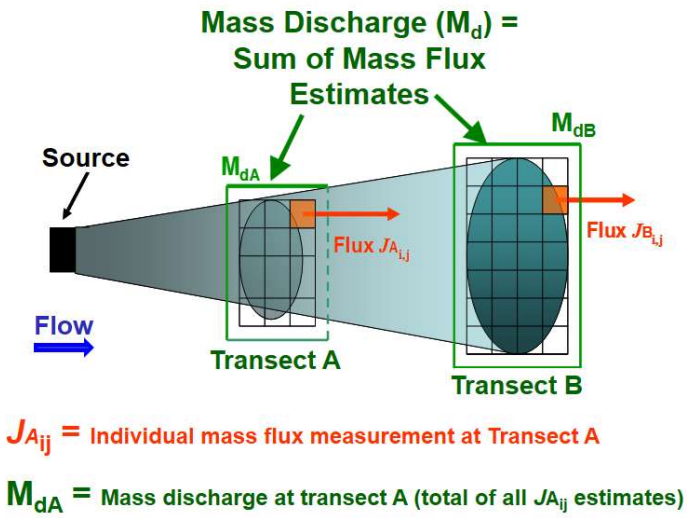

Figure 4. Concepts of Mass Flux (J) and Mass Discharge (M_d)
(Courtesy of Dr. Hans Stroo as reproduced in ITRC [2010])

Table 5. Calculation of Contaminant Mass Flux and Mass Discharge

$Contaminant\ Mass\ (J) = q \cdot C_W = -K \cdot i \cdot C_W$
q – Groundwater flux (L^3/L^2/T) ***K*** – Saturated hydraulic conductivity (L/T) ***i*** – Hydraulic gradient (unitless) ***C_W*** – Average aqueous concentration (M/L^3)
$Contaminant\ Mass\ Discharge\ (M_d) = \int_A J\, dA$
J – *Mass flux (M/T/L^2)* ***A*** – Area of the control plane or cross-section (L^2)

3.1 TOOLS FOR ESTIMATING MASS DISCHARGE

The methods used to estimate mass discharge are first described and then tools used to calculate this parameter are presented in Table 6.

3.1.1 Transect Methods

Five methods are used to calculate mass flux and/or mass discharge including:

- The transect method, which uses individual monitoring points to integrate concentration and flow data;
- Transects based on isoconcentration contours, which rely on isoconcentration contour maps developed using groundwater monitoring data;
- Passive flux meters, which estimate mass flux directly in wells along a transect;
- Well capture/pump test methods, which rely on extracting groundwater and measuring the flow and mass discharge from the wells; and
- Solute transport models.

The first three methods rely on measurements of the mass flux and/or mass discharge along a monitoring transect, while the remaining two methods rely on interpolation of pump test data and model simulations.

3.1.2 Mass Flux Toolkit

The Microsoft® Excel-based Mass Flux Toolkit was developed for the DoD (ESTCP Project ER-200430) to provide a tool for calculating mass discharge based on monitoring data collected for the transect method. The mass discharge is calculated based on measured concentrations of COCs at each monitoring well along a transect, hydraulic conductivity, and hydraulic gradient at each sampling point along the transect or as a single site-wide estimate.

The Mass Flux Toolkit can also be used to calculate mass discharge based on isoconcentration contours when monitoring data along a transect are not available at a site. In this case, existing isoconcentration contour maps are used to estimate concentration along a selected transect. The "monitoring points" correspond to the locations where the transect line intersects the isoconcentration contours. The concentration in the grid cell between monitoring points can be approximated by the arithmetic or geometric mean of the isoconcentration contour lines (GSI, 2006).

3.1.3 Solute Transport Models

Analytical and numerical solute transport models can also be used to calculate mass flux and mass discharge. Solute transport models require inputs of flow and concentration data. 3-D numerical solute transport models, such as MODFLOW/MT3D or MODFLOW/RT3DMS, can be used to

Table 6. Summary of Mass Discharge Tools

Tool	Scale		Data Inputs	Data Outputs	Pros	Cons	Additional Comments
	Source	Plume					
Isoconcentration Contour Method	X	X	• Concentration at monitoring wells • Isoconcentration contour map • Aquifer thickness, porosity • Distribution coefficient and soil bulk density (mass calculation) • Hydraulic conductivity and gradient (mass discharge calculation)	• Dissolved and sorbed contaminant mass • Mass discharge at select transects	• Relies on existing isoconcentration contour maps • Minimum data requirement • Easy and fast to implement • Estimate can be part of routine monitoring reports • Applicable to both source and plume scales	• Assumption of uniform properties • Low permeability zones are not taken into account	
Mass Flux Toolkit		X	• Concentration at monitoring wells along transect • Hydraulic conductivity and gradient	• Mass discharge along transect	• Excel-based • Includes evaluation of uncertainty, with possibility to run Monte-Carlo analysis		Development funded by DoD ESTCP
3-D Numerical Solute Transport Models	X	X	• Hydrostratigraphy • Hydraulic properties • Boundary conditions • Initial concentrations	• Concentration over time at any location in the domain • Mass discharge at select transect • Time to reach target contaminant mass, mass discharge or concentration	• Can take advantage of already existing 3-D models for the site • Can account for complex geology heterogeneity • Can account for complex processes, such as matrix diffusion, NAPL dissolution, complex degradation pathways	• Requires large amount of data • Can require significant level of effort to develop (time and money)	
Matrix Diffusion Toolkit	X	X	• Loading period, source concentration, length of time that release from low-permeability zone has occurred • Diffusion coefficient, tortuosity factor, porosity and sorption parameters in the low-permeability zone • Darcy velocity, hydraulic conductivity and gradient and degradation rate in the transmissive zone	• Mass discharge over time • Concentration in transmissive zone over time • Mass in transmissive zone over time • Aqueous, sorbed and total concentrations in low-permeability zone over time (Dandy-Sale Model only)	• Takes into account matrix diffusion • Provides mass estimates in both transmissive and low-permeability zones • Includes degradation in the transmissive zone • Includes evaluation of uncertainty, with possibility to run Monte-Carlo analysis • Can be calibrated with available monitoring data • Includes consideration of DNAPL removal in the source zone	• Estimates relies on significantly on the loading period and concentration during loading periods, which are difficult to estimate • Does not include degradation in the low-permeability zone, which can be an importance attenuation process • Cannot be used to estimate remediation timeframe for partial source mass removal	Development funded by DoD ESTCP

calculate the mass discharge at selected locations in a model domain. The development of 3-D numerical solute transport models generally requires a significant amount of data as well as model calibration. However, large-scale sites that warrant 3-D model development and/or sites with existing numerical models may benefit from utilizing the models to estimate mass discharge.

3.1.4 Matrix Diffusion Toolkit

The Microsoft® Excel-based Matrix Diffusion Toolkit (GSI, 2012), another type of solute transport model, computes the mass discharge. The models contained in this toolkit (i.e., the Square Root Model and Dandy-Sale Model) describe and calculate the mass discharge from a low-permeability zone to a transmissive zone, based on the inputs summarized in Table 6 and discussed in Section 2.1.3.

3.2 MASS DISCHARGE CASE STUDY: NAVAL AIR STATION NORTH ISLAND

Mass discharge evaluations were used at IR Site 5, Unit 2 Naval Air Station North Island, California to serve as a metric to evaluate natural attenuation processes. The mass removal of chlorinated ethenes via natural attenuation was estimated by calculating the amount of mass lost between two cross-sectional transects along the same flow path (both perpendicular to groundwater flow). The calculation was performed at two different points in time (July 1998 and July 2005). These dates represent the two periods with the highest concentrations of COCs and represent the same season. The locations of the selected transects along with isoconcentration contours generated from historical sampling data are shown in Figure 5. The upgradient transect, Flux Profile 1, dissects the area having the greatest COC concentrations. The downgradient transect, Flux Profile 2, is located approximately 175 feet downgradient and parallel to Flux Profile 1. The cross-sectional flow area at each transect was determined between each set of isopleth contours. It was calculated by multiplying the distance between the contours by the saturated thickness of the aquifer. The saturated thickness was estimated based on assumed aquitards to groundwater and solute migration. Groundwater flow through each flux profile was determined based on Darcy's Law using measured hydraulic gradients and conductivities. A water balance was performed to compare the total volume of water flowing through each transect to provide a degree of confidence that the water passing through the upgradient transect was being captured at the downgradient transect (Wiedemeier and Associates, 2006).

For July 1998, 16,900 gallons per day (gal/day) flowed across Flux Profile 1 and 16,000 gal/day flowed across Flux Profile 2 (95% capture). Similarly, for July 2005, 24,100 gal/day flowed across Flux Profile 1 and 24,900 gal/day flowed across Flux Profile 2 (97% capture). The mass flowrate through each transect was determined by multiplying the water flowrate by the arithmetic mean of the concentration between sets of two contours and summing the resulting values. An estimate of the amount of mass reduction between the two cross-sectional areas of flow was determined by subtracting the mass flowrate at the downgradient location from the mass flowrate at the upgradient location. The amount of chlorinated ethene mass lost using the July 1998 data was estimated to be about 8,400 lb/yr, and the mass lost using the July 2005 data was estimated to be about 8,800 lb/yr. Results were relatively consistent between the two periods and led to the conclusion that natural attenuation at the site is capable of removing significant contaminant mass. In addition, it was concluded that MNA would be sufficient to keep the solute plume from

migrating downgradient. Hence, the evaluation indicated that the application of a more aggressive and potentially costly remedy would not be necessary to contain the plume (Wiedemeier and Associates, 2006).

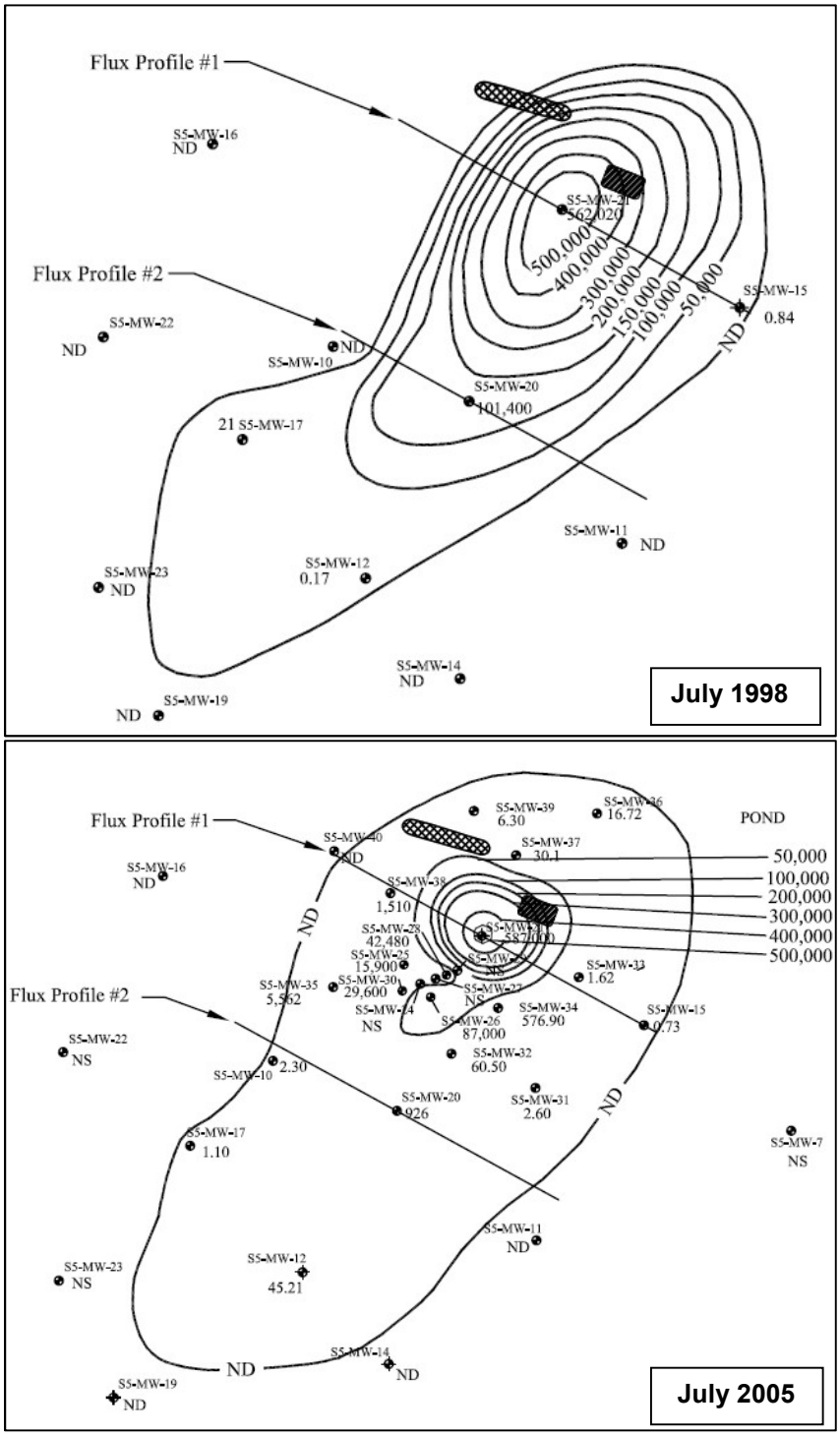

Figure 5. Mass Discharge Transect Maps (Courtesy of Wiedemeier and Associates, 2006)

4.0 REMEDIATION TIMEFRAMES

The remediation timeframe is the time required to reach a specific remediation performance metric. Examples of remediation performance metrics may include:

- Reaching a certain concentration target in the high-concentration source zone;
- Reaching a certain mass removal ratio or percentage in the high-concentration source zone;
- Reaching a certain concentration target in a downgradient receptor, such as a monitoring well; or
- Reaching a certain mass discharge target at a downgradient transect.

4.1 TOOLS FOR ESTIMATING REMEDIATION TIMEFRAMES

Contaminant mass and mass discharge estimates are the basis for developing remedial strategies and estimating associated remediation timeframes. As summarized in Table 7, several tools are available for estimating remediation timeframes for technologies such as monitored natural attenuation (MNA) and pump-and-treat systems.

4.1.1 Natural Attenuation Modeling

MNA is typically included in the evaluation of remedial alternatives for any given site. It is widely used either as a primary remediation technology or as the final "polishing step" in a treatment train process.

BIOCHLOR for chlorinated solvents (United States Environmental Protection Agency [U.S. EPA], 2002) and its companion model BIOSCREEN for petroleum hydrocarbons (U.S. EPA, 1997) are Microsoft® Excel-based tools that can be used to simulate contaminant concentrations downgradient of a source zone and estimate the timeframe to reach a target concentration at a specific point of compliance under natural attenuation. BIOCHLOR and BIOSCREEN simulate solute transport with and without biotransformation. Biotransformation of petroleum hydrocarbons can be simulated via first-order decay or instantaneous reaction in BIOSCREEN, while biotransformation of chlorinated solvents is simulated as sequential first-order decay uniformly or in two different reaction zones in BIOCHLOR. The data input screens for BIOCHLOR and BIOSCREEN are shown in Figures 6 and 7, respectively. A number of site-specific hydrogeologic, contaminant, and biogeochemical data must be entered into the model. Of particular importance are hydraulic conductivity and gradient, which are used by the model to calculate seepage velocity. Other input parameters include, but are not limited to contaminant concentrations, partitioning coefficients, and concentrations of terminal electron acceptors (BIOSCREEN). The contaminant concentrations are required for groundwater monitoring wells located various distances downgradient from the source. Biotransformation rate constants can be entered and compared to model-generated concentration versus distance plots. The rate constants are then varied until the resulting curves match the field data at which time the rate constants are assumed to be representative of field conditions.

Table 7. Summary of Remediation Timeframe Tools

Tool	Scale		Data Inputs	Data Outputs	Pros	Cons	Additional Comments
	Source	Plume					
SourceDK	X		Mass Estimate • Method 1: Average soil concentration, volume of source zone ad soil bulk density • Method 2: Extent of NAPL zone, soil bulk density, measured soil concentrations in NAPL zone, porosity, measured dissolved concentrations, distribution coefficient and soil bulk density • Method 3: NAPL saturation, porosity, volume of NAPL zone and density of NAPL source Remediation Timeframe • Initial concentration, desired cleanup level, source zone length, seepage velocity, retardation factor, and if NAPL constituents, type of media, density of NAPL fluid, NAPL saturation and seepage velocity under pumping conditions	• Mass versus time charts • Number of pore volumes and time required to achieve desired cleanup level	• Provides four averaging methods to compute average soil/aqueous concentrations • Excel-based • Can account for effect of pumping	• Does not account for matrix diffusion when calculating number of pore volumes required to achieve cleanup • Only applicable to the source zone	Development funded by AFCEE
Matrix Diffusion Toolkit	X	X	• Loading period, source concentration, length of time that release from low-permeability zone has occurred. • Diffusion coefficient, tortuosity factor, porosity and sorption parameters in the low-permeability zone • Darcy velocity, hydraulic conductivity and gradient and degradation rate in the transmissive zone	• Mass discharge over time • Concentration in transmissive zone over time • Mass in transmissive zone over time • Aqueous, sorbed and total concentrations in low-permeability zone over time (Dandy-Sale Model only)	• Takes into account matrix diffusion • Provides mass estimates in both transmissive and low-permeability zones • Includes degradation in the transmissive zone • Includes evaluation of uncertainty, with possibility to run Monte-Carlo analysis • Can be calibrated with available monitoring data • Includes consideration of DNAPL removal in the source zone	• Estimates rely significantly on the loading period and concentration during loading periods, which are difficult to estimate • Does not include degradation in the low-permeability zone, which can be an importance attenuation process • Cannot be used to estimate remediation timeframe for partial source mass removal	Development funded by DoD ESTCP

Table 7. Remediation Timeframe Tools (continued)

Tool	Scale		Data Inputs	Data Outputs	Pros	Cons	Additional Comments
	Source	Plume					
3-D Numerical Solute Transport Models	X	X	• Hydrostratigraphy • Hydraulic properties • Boundary conditions • Initial concentrations	• Concentration over time at any location in the domain • Mass discharge at select transect • Time to reach target contaminant mass, mass discharge or concentration	• Can take advantage of already existing 3-D models for the site • Can account for complex geology heterogeneity • Can account for complex processes, such as matrix diffusion, NAPL dissolution, complex degradation pathways	• Requires large amount of data • Can require significant level of effort to develop (time and money)	
BIOCHLOR & BIOSCREEN		X	• Seepage velocity • Dispersivity parameters • Sorption parameters • Source geometry, source concentration, source decay rate • Plume biotransformation rates	• Concentration over time in plume • Plume mass with and without biotransformation	• Developed and approved by US EPA • Excel based • Includes decaying source • Includes biotransformation (including sequential decay for chlorinated solvents) • Possible to define two reaction zones in the plume • Can be calibrated with available monitoring data	• Assumes uniform, one directional flow field • Cannot directly account for pumping • Cannot account for partial/complete source removal • Cannot account for matrix diffusion in the source or plume	Development funded by US EPA
Natural Attenuation Software (NAS)	X	X	• Hydraulic conductivity/gradient • Total/effective porosity • Sorption parameters • Source concentration, source width/length • Redox indicators • NAPL properties	• Distance of plume stabilization • Time of stabilization • Time of NAPL dissolution	• Accounts for both source and plume zones • Advanced features such as redox zonation and alternate degradation pathways • Can account for the effect of pumping • Can simulate NAPL dissolution in source area	• Numerical simulations require for NAPL dissolution • Significant run times might be required for numerical simulations	Development funded by Naval Facilities Engineering Command (NAVFAC)
REMChlor / REMFuel		X	• Seepage velocity • Dispersivity parameters • Sorption parameters • Source geometry, source concentration, source decay rate • Source removal fraction and time • Plume biotransformation rates	• Concentration over time in plume • Mass discharge over time in plume • Cancer risks over time	• Developed and approved by US EPA • Includes decaying source • Include partial/complete source removal • Includes biotransformation (including sequential decay for chlorinated solvents) • Possible to define three reaction zones and three reaction periods for the plume • Can indirectly account for matrix diffusion in the source • Can be calibrated with available monitoring data	• Assumes uniform, one directional flow field • Cannot directly account for pumping • Relies on empirical exponent for power-function relationship • Cannot account for matrix diffusion effects in the plume	Development funded by US EPA. An updated version is currently under development called REMChlor-MD that simulates plume transport with matrix diffusion and includes enhanced degradation as a function of space and time in both the high and low permeability zones (ER-201426).

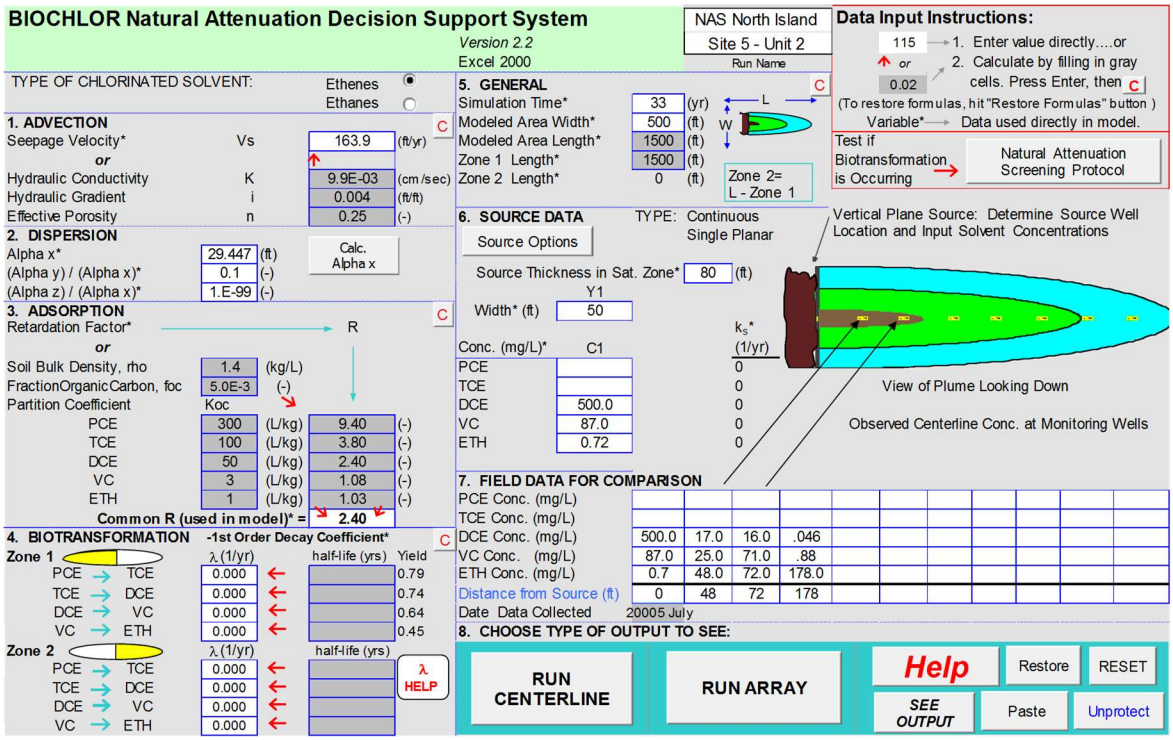

Figure 6. BIOCHLOR Input Parameters (Courtesy of AFCEE)

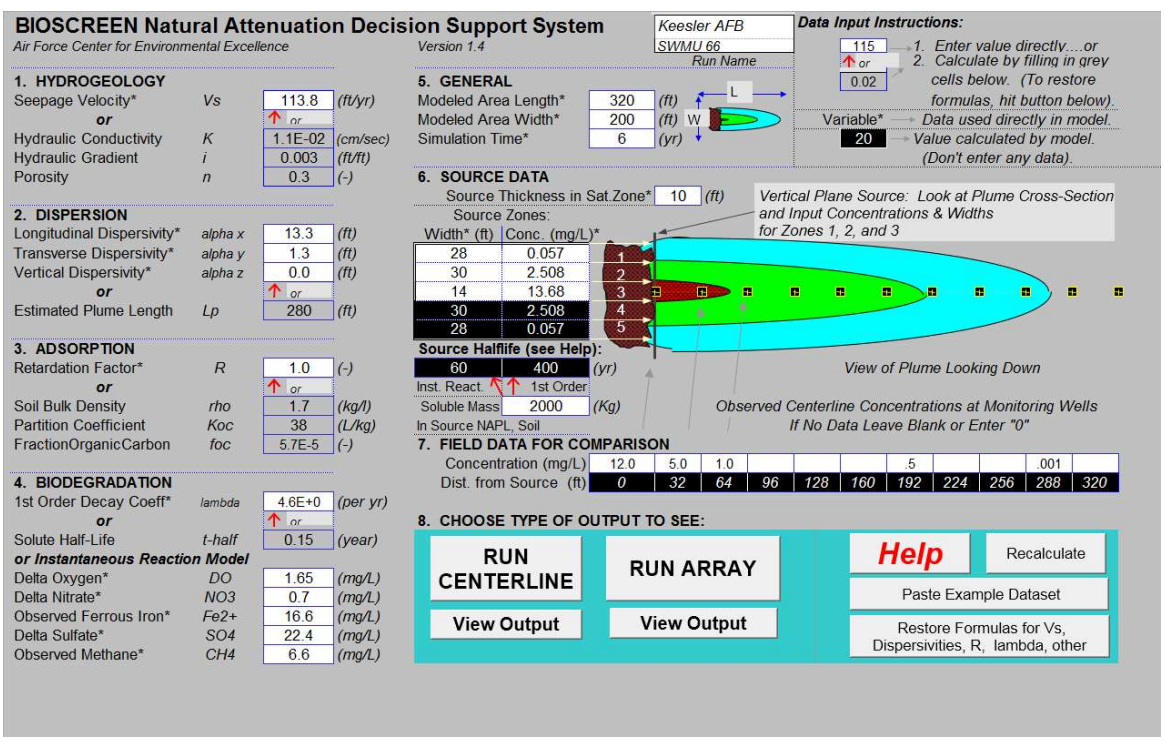

Figure 7. BIOSCREEN Input Parameters (Courtesy of AFCEE)

Natural Attenuation Software (NAS) (Chapelle et al., 2003) uses a combination of analytical and numerical solute transport models to estimate remediation timeframes and assist in decision-making for source treatment (source mass removal) required to meet specific performance objectives. NAS provides estimates for:

- Distance of plume stabilization (DOS), which corresponds to the distance it will take for an aquifer to reduce (e.g., via natural biodegradation, sorption, advective mixing, etc.) the contaminant concentrations to a target concentration specified by the user. Based on this estimate, NAS can be used to estimate the source target concentration necessary to reach a specific target concentration at a downgradient point of compliance;
- Time of stabilization (TOS), which corresponds to the time it takes for a plume to shrink to a smaller configuration if a contaminant source is wholly or partially removed (Figure 8);
- Time of remediation (TOR), which corresponds to the time it takes to attain a remedial goal at a specific compliance point; and
- Time of NAPL dissolution (TOD), which corresponds to the time it takes for NAPL in a source area to dissolve and for contaminant concentrations to decrease to reach a target dissolved concentration level.

DOS, TOR and TOS are calculated based on an analytical solution and require the user to enter estimates of the hydraulic properties, sorption parameters, source characteristics, saturated thickness impacted by contamination, and redox indicators. TOD is calculated based on numerical simulations and therefore might require longer durations to run the model. TOD evaluations also require additional input parameters such as NAPL properties (e.g., composition and mass).

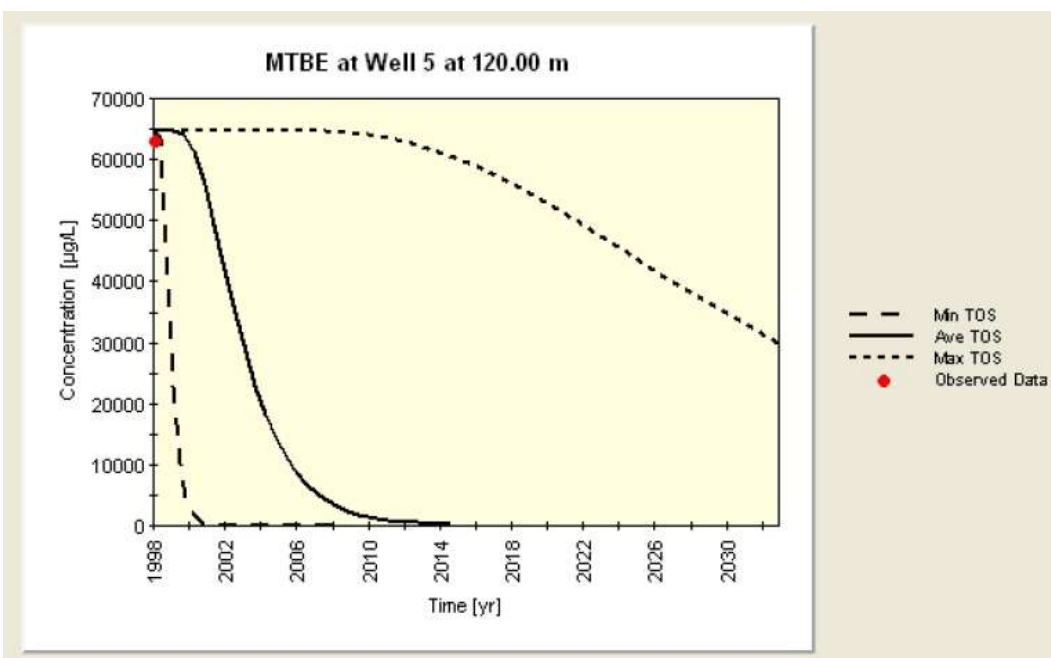

Figure 8. NAS Output for TOS Calculation for an MTBE Plume (Courtesy of Widdowson et al., 2005)

4.1.2 Matrix Diffusion Toolkit

The Microsoft® Excel-based Matrix Diffusion Toolkit (GSI, 2012) can be used to estimate remediation timeframes at sites where matrix diffusion is an important part of the CSM. Both models (Dandy-Sale and Square Root) in the Matrix Diffusion Toolkit can be used to simulate concentration over time in a source zone following NAPL removal. An example screenshot of the data input window for the Square Root Model is shown in Figure 9. The time to achieve a specific concentration level at a chosen point of compliance is the remediation timeframe. The Matrix Diffusion Toolkit allows the user to account for degradation in transmissive zones, but not in low-permeability zones. See Section 2.1.3 for more information on this toolkit.

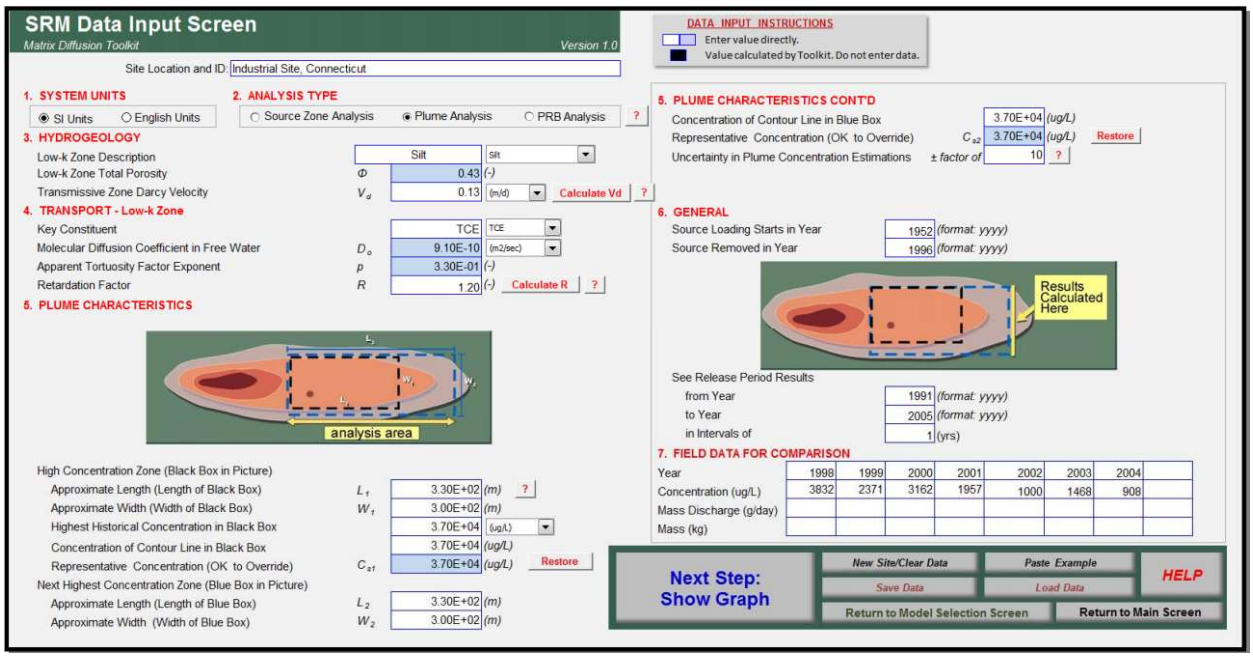

Figure 9. Data Input Screen for the Square Root Model (Courtesy of GSI, 2012)

4.1.3 REMChlor/REMFuel

REMChlor (U.S. EPA, 2007) and REMFuel (U.S. EPA, 2012) simulate source and plume remediation for chlorinated solvents and petroleum hydrocarbons, respectively, based on analytical solutions. Specifically, these tools can be used to estimate remediation timeframes, as the time to achieve target concentration at a downgradient point of compliance, for different source mass removal alternatives. Natural attenuation and/or enhanced degradation can be accounted for in the plume with up to three degradation zones and three degradation periods with different decay rates. The data inputs for these tools are source characteristics (mass, concentration, source width/depth, exponent for power-function relationship), source remediation parameters (fraction removed, remediation period, and first-order decay), characteristics of the degradation zones and periods (decay rates, zone length, and decay time periods), and transport parameters (retardation factor, velocity, and dispersivity values).

4.1.4 SourceDK

The SourceDK tool can be used to estimate the remediation timeframe to achieve a specific target concentration in the source area under natural dissolution or pump-and-treat conditions (GSI, 2011). The source remediation timeframe is based on the number of pore volumes required to flush out the constituent from the source area to reach a specific cleanup concentration. The "Tier 3 Process Model" in SourceDK calculates the requisite number of pore volumes and corresponding remediation timeframe. An example of the output generated is shown in Figure 10. See Section 2.1.2 for more information on this tool.

Figure 10. SourceDK Output Screen for a Petroleum Refinery Site (Courtesy of GSI, 2011)

4.1.5 Solute Transport Modeling

3-D numerical solute transport models, such as MODFLOW/MT3D or MODFLOW/RT3DMS, can be used to simulate a range of remedy alternatives (e.g., different percentages of source mass removal or different pump-and-treat configurations). Remediation timeframes can also be estimated for various cleanup objectives such as target mass discharge or target concentration at a downgradient receptor.

4.2 REMEDIATION TIMEFRAMES CASE STUDY: FORMER NAVAL AIR STATION ALAMEDA

Two NAS models were constructed to evaluate the potential for MNA at Site 14 Former Naval Air Station Alameda, California after applying ISCO to treat DCE and VC, the primary COCs at the site. NAS was selected because of its ease of use to provide a screening level estimate of

remediation timeframe for natural attenuation to achieve remedial goals. First, the stability of the remaining chlorinated ethenes was evaluated to determine: 1) if the remaining areas above the institutional control (IC) termination criterion were stable, and 2) if so, what distance would be required to achieve the IC termination criterion. Second, the TOR was evaluated at Site 14 to predict the time to reach the IC termination criterion throughout the site.

Two transects through the site were selected for the NAS model runs: one to estimate the DOS and the other for estimation of the TOR (Figure 11). The DOS transect was selected to represent the "worst case scenario" for the remaining areas above the IC termination criterion. The highest concentration of VC measured in July 2010 was observed at M14-15. The remaining monitoring wells included in this transect were selected because they represent a potential downgradient flowpath for groundwater contamination from M14-15. The TOR transect passed through the southernmost portion of the treatment area and extended through a remaining hot spot centered around monitoring well M14-09. As with the DOS transect, the TOR transect began at the well with the highest VC concentration (M14-06) and followed a potential groundwater flowpath through the site.

NAS input parameters included hydraulic conductivity, hydraulic gradient, porosity, groundwater velocity, concentrations of COCs, and geochemical parameters including iron, manganese, and dissolved oxygen. The hydrogeology data was the same for each transect. The contaminant and redox indicators varied for each transect based on specific monitoring well data.

The result of the DOS analysis (Figure 12) indicated that the IC termination criterion would be met within 15 m (50 ft) of monitoring well (M14-15), and hence there were no concerns regarding lateral migration of the plume or interactions with the nearby surface water. Results also indicated that no additional source removal would be required to meet the IC termination criterion for the DOS "worst case" transect, and that all remaining areas of contamination would be stable. These results reinforced the success of the ISCO application at the site and supported the transition from ISCO to MNA.

Results of the TOR analysis provided a range of estimated TORs based on hydraulic properties and estimated total chlorinated ethene concentration remaining in a transect. The TOR analysis for the TOR transect shown in Figure 11 predicted the time to reach the IC termination criterion to range from 2.5 to 5.7 years with an average of 3.6 years. For comparison purposes, a TOR analysis was completed for the DOS transect. The DOS transect predicted a similar average time to reach the IC termination criterion, having an average TOR of 2.9 years with minimum and maximum TORs ranging from 2.1 to 4.8 years, respectively. This information was valuable for assessing life-cycle cost for the remainder of the remedy, as well as for planning future land use.

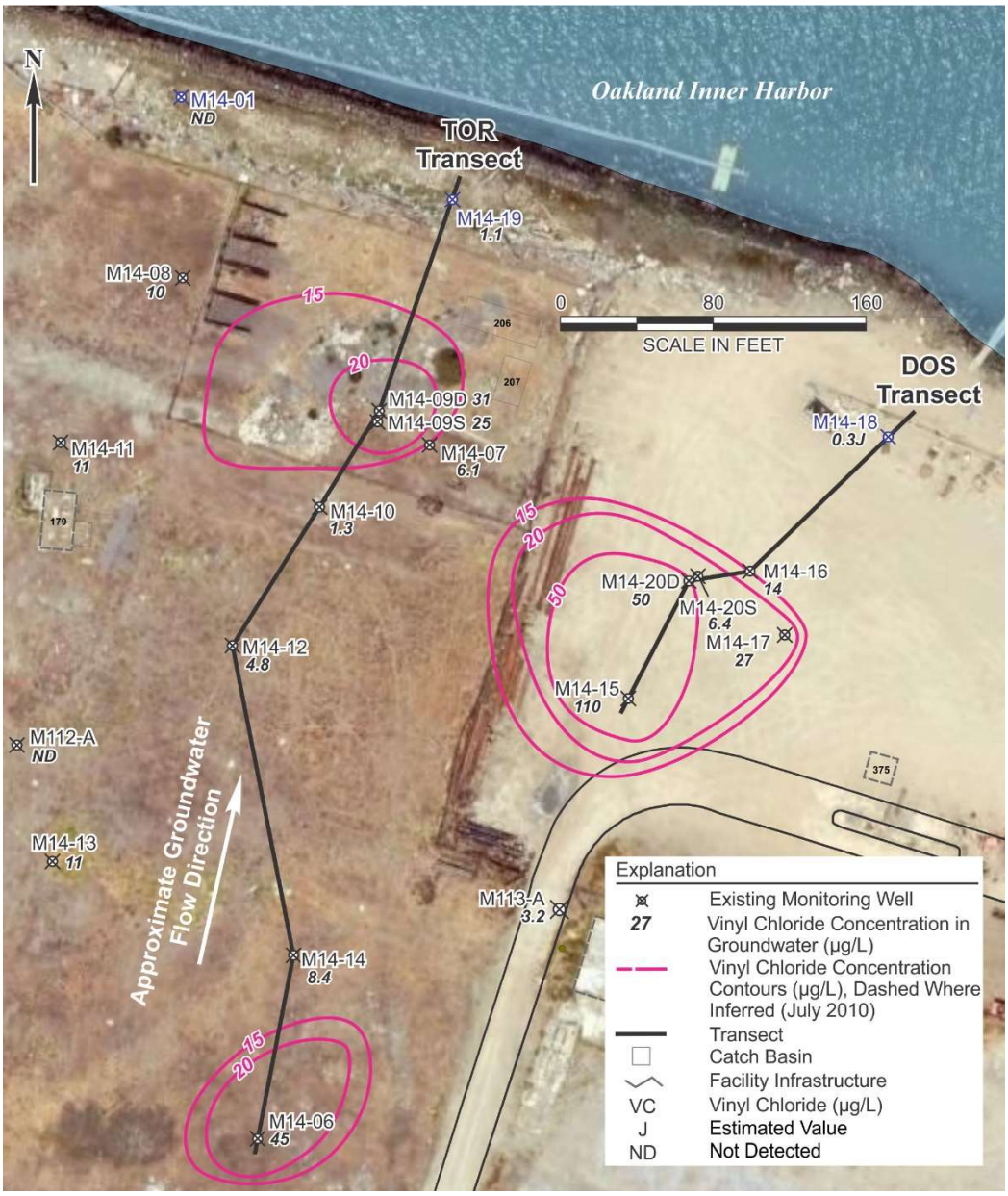

Figure 11. DOS and TOR Transects Used for NAS Modeling at Site 14, Former Naval Air Station Alameda (Courtesy of Battelle)

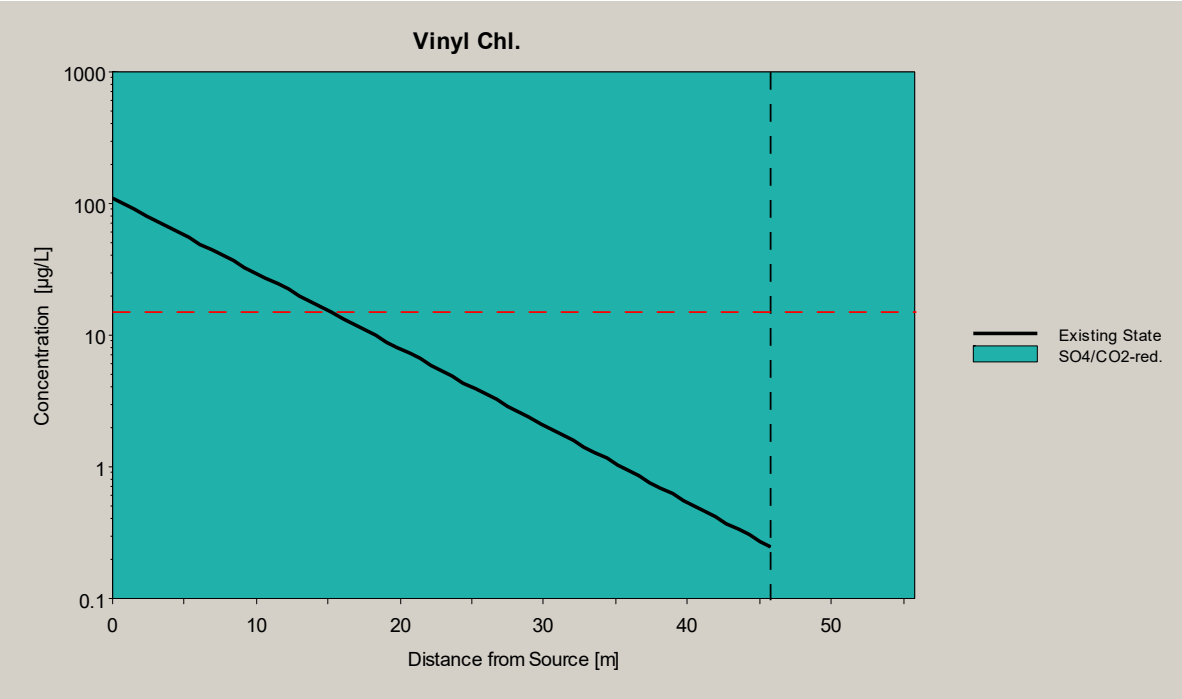

Figure 12. DOS Analysis for the IC Termination Criterion (Red dashed line) (Courtesy of Battelle)

5.0 CONCLUSIONS

A wide range of tools are available to assess contaminant mass-in-place, mass discharge, and remediation timeframes. Several of the Microsoft® Excel-based tools are user-friendly, menu driven, and developed for use by DoD and other end-users at no charge. Additional information is provided in Section 6.0 to download these tools. All of the tools described in this document can be applied using a typical personal computer. While some tools presented herein can be used for multiple applications, most of the tools are specific and therefore a combination of tools may be useful in the development of the CSM and to inform the remedial decision-making process.

6.0 RESOURCES

BIOSCREEEN:	https://www.epa.gov/water-research/bioscreen-natural-attenuation-decision-support-system
BIOCHLOR:	https://www.epa.gov/water-research/biochlor-natural-attenuation-decision-support-system
Matrix Diffusion Toolkit	https://www.serdp-estcp.org/Tools-and-Training/Environmental-Restoration/Groundwater-Plume-Treatment/Matrix-Diffusion-Tool-Kit
Natural Attenuation Software (NAS):	http://www.nas.cee.vt.edu/index.php
REMChlor:	https://www.epa.gov/water-research/remediation-evaluation-model-chlorinated-solvents-remchlor
REMChlor-MD:	https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Persistent-Contamination/ER-201426/ER-201426/(language)/eng-US
REMFuel:	https://www.epa.gov/water-research/remediation-evaluation-model-fuel-hydrocarbons-remfuel
SourceDK:	https://clu-in.org/products/dst/DST_Tools/SourceDK.htm

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