

REMChlor-MD Toolkit

USER'S MANUAL

Version 1.0
ESTCP ER-201426
June 2018

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CITATION

Falta R.W., Farhat, S.K., C.J. Newell, and K. Lynch, 2018. REMChlor-MD, developed for the Environmental Security Technology Certification Program (ESTCP) by Clemson University, Clemson, South Carolina and GSI Environmental Inc., Houston, Texas.

Farhat, S.K., C.J. Newell, R.W. Falta, and K. Lynch, 2018. REMChlor-MD User's Manual, developed for the Environmental Security Technology Certification Program (ESTCP) by GSI Environmental Inc., Houston, Texas and Clemson University, Clemson, South Carolina.

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REMCHLOR-MD TOOLKIT
Environmental Security Technology Certification Program

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QUICK START

What is REMChlor-MD?

A new version of the REMChlor (Falta *et al.*, 2007) model with the ability to simulate matrix diffusion processes in the *plume* (matrix diffusion was already considered in the *source* term in the REMChlor model).

Matrix Diffusion?

Low-k zones (low permeability zones such as silt, clay layers) can serve as indirect, low-level sources of contamination to transmissive zones due to matrix diffusion. If you can apply several simplifying assumptions about heterogeneity and a site's concentration history to your site, REMChlor-MD can provide planning-level estimates of:

- Concentration, mass, and mass discharge (sometimes called mass flux, in grams per day) in the transmissive zone caused by matrix diffusion before or after remediation;
- Mass of contaminants at any time in the low-k zone; and
- Concentration at any time in an observation well.

Why Is This Important?

Understanding and evaluating matrix diffusion can provide supporting information regarding a variety of key questions, such as:

1. If I remediate a transmissive zone, but my remediation technology doesn't remove contaminants from low-k zones in contact with the transmissive zone, will I be able to achieve my cleanup standards?
2. How much contaminant mass could be present in low-k zones at my site?
3. If I install a permeable reactive barrier, will I have trouble achieving cleanup standards downgradient of the barrier?
4. If I remove all the DNAPL from a source zone, is there a chance groundwater concentrations will remain above MCLs?
5. How much longer might I have to wait for a source zone to achieve MCLs after the DNAPL is all gone?

Do I Need Special Sampling Data from Low-k Zones?

If you want to learn more about the potential impacts of matrix diffusion, or want planning-level modeling results, then the REMChlor-MD tool can be applied without sampling data from the low-k zones. The Toolkit can provide useful information about the *general* trends or style of matrix diffusion effects, but *absolute* values of the results may vary considerably from actual results. The accuracy of the modeling results will be increased if there are data from the low-k zones that can be used to calibrate the models in the tool. (For more information about matrix diffusion see Sale *et al.*, 2013, SERDP Project ER-1740.)

What Input Data Will I Need?

Some of the input data are similar to what is used for existing solute transport models: Darcy groundwater velocity, size of the modeled area, information on when the source started, etc. Other input data will look new to most users; for example, you'll need to estimate the tortuosity of the low-k materials where matrix diffusion has occurred, diffusion coefficients, fraction organic carbon of the clays and silts being modeled. REMChlor-MD provides default values and advice on how to pick the best value that represents your site conditions.

INTRODUCTION

Restoration at current and former military installations is expected to cost the U.S. Department of Defense (DoD) more than ten billion dollars. Many of these sites contain groundwater that is contaminated by chlorinated volatile organic compounds (CVOCs), often in the form of dense non-aqueous phase liquids (DNAPLs). DNAPLs serve as concentrated sources of groundwater contamination from which most dissolved CVOC plumes originate. Considering that source concentrations can be four or five orders of magnitude greater than maximum contaminant levels (MCLs), restoration of source zones to pristine conditions is difficult; however, reduction of CVOC plumes is a realistic goal that may be achieved through various combinations of source and plume remediation. Much research over the past two decades has focused on technology development for both source and plume remediation at sites contaminated by CVOCs.

Unfortunately, some CVOC sites have proven to be exceedingly difficult to address due to the phenomenon of **matrix diffusion (Figure 1)**. Matrix diffusion occurs when CVOCs diffuse from high permeability zones into adjacent low permeability zones during a “loading period.” This loading period is followed by a “release period,” during which the contaminants in the low permeability zones gradually diffuse back into the high permeability zones (Parker *et al.*, 1994; 1997; Ross and Lu, 1999; Slough *et al.*, 1999; Esposito and Thompson, 1999; O’Hara *et al.*, 2000; Reynolds and Kueper, 2001; 2002; 2004; Liu and Ball, 2002; Parker *et al.*, 2004; Falta, 2005; Chapman and Parker, 2005; Parker *et al.*, 2008; Sale *et al.*, 2008). This process may occur in any heterogeneous setting, but it is particularly important in certain fractured bedrock sites, and in sites with extensive clay lenses or layers. These types of complex site conditions tend to produce plumes that are long lived, requiring long-term monitoring.

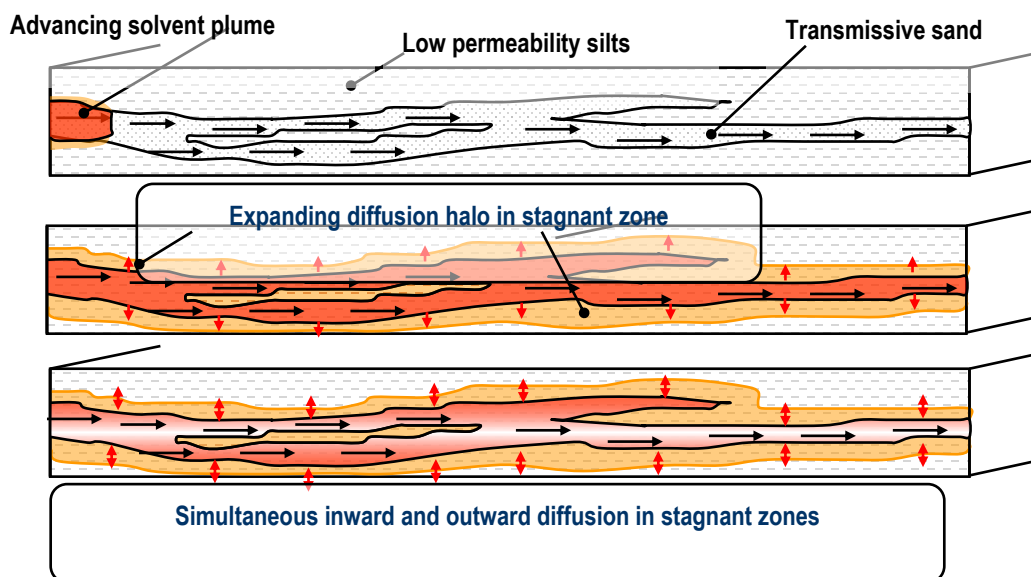


Figure 1: Conceptual Model of matrix diffusion effects as part of plume response.
(Source: T. Sale, T. Illangasekare, AFCEE, 2007)

While matrix diffusion has been identified as a potential problem at complex fractured and heterogeneous environments, there are relatively few tools available to help practitioners in the field determine if matrix diffusion could be a problem at their site. The ESTCP's Matrix Diffusion Toolkit (Farhat *et al.*, 2012) is currently the only software tool available that is specifically designed to evaluate matrix diffusion effects at contaminated sites. Note that many conventional numerical models (such as MODFLOW/MT3D) have difficulty simulating matrix diffusion effects unless very high-resolution grids are used (e.g., on the order of centimeters) (Rasa *et al.*, 2011; Chapman *et al.*, 2012), making the modeling process impracticable for many three-dimensional field scale modeling projects.

To better equip the groundwater community with cost-effective, accessible, useable, and practical tools for addressing CVOC contamination in complex fractured and heterogeneous environments, the DoD's Environmental Security Technology Certification Program (ESTCP) has funded the development of the REMChlor-MD tool (Toolkit) through project ER-201426.

REMChlor-MD was developed as a cost-effective management tool for addressing contamination in a broad range of geological settings, including fractured porous media, heterogeneous media with low permeability inclusions, and high permeability zones that are adjacent to low permeability aquitards. The Toolkit allows the accounting of several types of source and plume remediation activities. This should permit the management tool to be used to make informed decisions on remediation technology application and optimization.

Programmed for Microsoft Excel 2016, separate REMChlor-MD versions are provided for the 32-bit and 64-bit versions of Excel.

INTENDED USES AND LIMITATIONS FOR REMCHLOR-MD

REMChlor-MD attempts to assist site managers and site consultants better understand matrix diffusion and help site stakeholders determine if matrix diffusion processes are significant enough to cause “rebounding” of downgradient plume concentrations above remediation goals after plume remediation or isolation is complete. Having this information readily available before a remedy is implemented, could assist site stakeholders select more appropriate remedies and improve effective risk communication with regulators and the public.

REMChlor-MD is intended to be used as a **screening level tool** for simulating matrix diffusion effects. REMChlor-MD has the following assumptions and limitations:

- Assumes the user is familiar with basic groundwater transport and mass balance concepts.
- Assumes a homogeneous and constant groundwater velocity field with flow in only one direction.
- The contaminant source mass balance assumes that the contaminant discharge is a power function of the remaining contaminant mass using an exponent Γ (gamma). As a simplistic model of a complicated heterogeneous multiphase transport system, the best value of gamma for a given site will be subject to a range of uncertainty. For this reason, it is probably a good idea to run the model with a range of gamma values.
- The model assumes that biodegradation reactions in the plume can be described by first order decay reactions. Biogeochemical conditions that control these reactions may not be well represented by first order reactions therefore, there is considerable uncertainty in values of field scale decay rates.
- First order decay rates are a function of time and distance from the source (x), but they do not depend on the y or z coordinates. This means that a specified reaction zone will extend over the entire model domain in the y and z directions.
- In the transmissive zone, the model uses a conventional advection-dispersion formulation. However, in the absence of matrix diffusion, this may not accurately represent the physical process at a site (e.g., see Hadley and Newell, 2014). There is a developing conceptual model that suggests that dispersion processes are much weaker than is commonly simulated, and that lower dispersion coefficients should be used in conventional advection dispersion models. By applying this model to a transmissive zone that only occupies part of the overall volume, and by including matrix diffusion, the transport can better fit the newer conceptual model.
- The matrix diffusion approach applied to the plume is new and has not been tested at a large number of sites. However, this model has been extensively verified with analytical and numerical solutions, and experimental laboratory data.

FREQUENTLY ASKED QUESTIONS

These comparisons are shown in Falta and Wang (2017) and Muskus and Falta (2018).

FREQUENTLY ASKED QUESTIONS

Why is matrix diffusion important? Won't the DNAPL take so long to go away that matrix diffusion will never be that important?

Matrix diffusion can be a key process both at sites where remediation has not been conducted, and at sites where much of the DNAPL has been removed by active remediation projects:

- For the no remediation case, a modeling study of small hypothetical 675 kg DNAPL release showed that it would take about 39 years for the DNAPL to dissolve away naturally, and then it would take another 87 years until matrix diffusion went below a certain source strength (0.1 grams per day) (Seyedabbasi *et al.*, 2012). This helps support the contention that there are a number of “Late Stage” chlorinated solvent sites where DNAPL is a relatively small part of the source, and matrix diffusion is the predominate or only contributor (Sale *et al.*, 2008a,b). Obviously if there is a very large DNAPL release of hundreds of thousands of pounds, then DNAPL will likely be a large part of the site conceptual model for a long time period.
- For the remediation case, there are perhaps thousands of sites where active in-situ remediation has removed DNAPL from the transmissive zone in the source and/or plume, but has left contaminants in the low-k zones behind. These sites are likely to be dominated by matrix diffusion effects now or sometime in the near future.

What is a Low-k Zone? Do I have these zones at my site?

Based on her research program at the University of Guelph, Dr. Beth Parker developed a rule of thumb indicating that matrix diffusion can be an important process, if there is a plume in a transmissive zone that is in contact with adjacent zones that have lower permeability by a factor of 100 or more. In other words, if a contaminant plume moving in a 10^{-3} cm/sec sand is in contact with a 10^{-5} cm/sec silt, then the silt can be charged up with contaminants during a loading period (when concentrations in the sand are higher than the silt) and then slowly discharge contaminants into the sand via diffusion when the silt has higher concentrations than the sand. Most hydrogeologic settings, even sites that are considered homogenous (such as a homogeneous sand), will likely exhibit some type of matrix diffusion effect during the site life cycle.

Does REMChlor-MD model matrix diffusion in both the source zone and the plume?

Yes, but in different ways. In the original REMChlor model, users can simulate matrix diffusion effects in the source zone by adjusting the “gamma” factor that controls the relationship between the mass discharge leaving the source and the mass remaining in the source over time. For example, entering a gamma of 1 or higher will produce a “long tail” in the mass discharge and concentration vs. time leaving the source that is seen at sources controlled by matrix diffusion. But the original version of REMChlor did not simulate matrix diffusion in the plume, leading to over optimistic cleanup scenarios in some cases.

This new version of REMChlor, REMChlor-MD, now allows users to enter hydrogeologic data from their site that will indicate how matrix diffusion in the plume will affect cleanup scenarios.

Can REMChlor-MD be used with fractured rock sites?

Yes. The REMChlor-MD can be used for simplified fractured rock sites assuming parallel fractures. Note, if you have both vertical and horizontal fractures that form blocks in the aquifer, then REMChlor-MD cannot handle this directly. However, the parallel fracture solution should provide answers that are relatively close.

What contaminants can be modeled with the REMChlor-MD?

To date, most of the research involving matrix diffusion for low-k zones has focused on chlorinated solvents such as TCE (trichloroethene) with a few projects focused on methyl-tert butyl ether (MTBE). However, in theory, matrix diffusion processes should apply to almost any dissolved contaminant, including per- and polyfluoroalkyl substances (PFAS) compounds and hydrocarbons, although the overall impacts may differ. Matrix diffusion of dissolved metals and radionuclides could also be modeled if a simplifying assumption of linear sorption/desorption relationship can be applied.

What type of questions will REMChlor-MD provide supporting information for?*

- How long will it take me to reach my cleanup goals in the plume under a Monitored Natural Attenuation scenario?
- Can I reach my remediation goals in the plume more quickly if some type of active remediation or a barrier is implemented in the source zone?
- Can I reach my remediation goals in the plume more quickly if some type of active remediation is performed in the plume?
- If I remediate the plume with a remediation technology that only treats the transmissive zone, will I see concentration rebound when the treatment stops?
- Do I get more benefit treating the source or the plume?
- Is it likely my plume is expanding, stable, or shrinking?
- Will the generation of daughter products in the plume be a problem?
- What is the mass flux / mass discharge at a certain point downgradient of the source?

** (Note, there is considerable uncertainty in any groundwater transport model, therefore modeling results should be used as a line of evidence rather than a 100% reliable prediction).*

At what type of site is REMChlor-MD going to matter and improve modeling predictions?

- Long plumes in heterogeneous hydrogeologic settings.
- Plumes that are receding because the source has been cut off or where source remediation has reduced the concentration and mass discharge leaving the source.
- Plumes with concentrations that are an order of magnitude more than the cleanup standard.

At what type of site will the new REMChlor-MD model have less impact compared to the conventional REMChlor model?

- Sites where the source and the plume are being managed by Monitored Natural Attenuation and matrix diffusion is already incorporated in the source “gamma” term.
- Sites with extensive degradation processes in the plume transmissive zone that quickly degrade any contaminants diffusing out of the low-k zone.

Can REMChlor-MD be used at LNAPL sites?

Yes, it can be used for LNAPL and many other types of sites. In theory matrix diffusion processes observed at chlorinated solvent sites will be applicable to LNAPL sites. However, we are not aware of any detailed research studies where matrix diffusion at LNAPL source zones was evaluated. Note that one group documented matrix diffusion effects associated with a MTBE/TBA plume (Rasa *et al.*, 2011), but this was not in an LNAPL source area.

Is REMChlor-MD able to simulate degradation in the low-k zone?

Yes. Currently, however, there is limited information on what the degradation rates should be; see SERDP ER-1740 project (Sale *et al.*, 2013) Section 4.3 for more details. This is a very sensitive factor in modeling; even a little degradation in the low-k zones can have significant implications on future concentrations (see SERDP ER-1740 project (Sale *et al.*, 2013) Section 5 for more details).

Why are there 32-bit and 64-bit versions of REMChlor-MD?

Most current personal computers use the 64-bit Windows Operating System. However, Excel 2016 is available as either a 32-bit or 64-bit version. The 32-bit version is the default installation. The Excel 2016 version (32 or 64-bit) can be found in Excel under Account – About Excel.



REMChlor-MD SEMI-ANALYTICAL MODEL

REMChlor-MD allows for efficient modeling of matrix diffusion in aquitards, layered and heterogeneous systems, and rock systems with parallel fractures. Using an alternative modeling approach, the tool employs semi-analytical approximations inside each normal (large) numerical gridblock to represent matrix diffusion at the local-scale. Originally developed in the geothermal reservoir modeling field for simulating transient heat conduction in low-k cap rocks, the method has been adapted to apply to matrix diffusion in aquifer aquitard systems, as well as in layered, heterogeneous, and fractured media, and includes daughter product generation in the low permeability zone. With this method, only the high permeability zone is discretized in the numerical model, and the interaction with the low-k zone is accounted for in a time-dependent source/sink term that is computed analytically in each gridblock at each time-step.

REMChlor-MD provides planning-level estimates of the concentration, mass, and mass discharge in the transmissive zone, concentration in an observation well, and mass in the low-k zone.

Governing equations and assumptions are provided in [Appendices 1 through 6](#). Guidelines for selecting key input parameters for the model are outlined in [Data Entry](#). For help on results, see [REMChlor-MD Results](#). Detailed descriptions of the mathematical approach and model verification are provided in Falta and Wang (2017) and Muskus and Falta (2018).

DATA ENTRY

Data Input Screen
Results

Three important considerations regarding data input are:

- 1) To see the example data set in the input screen of the software, click on the *Paste Example* button on the lower right portion of the input screen. The example dataset used in the Toolkit is similar to Tutorial 7 of the original REMChlor model, but includes matrix diffusion.
- 2) Because the REMChlor-MD tool is based on the Excel spreadsheet, you must click outside of the cell where you just entered data or hit *Return* before any of the buttons will work. Additionally, **REMOVING OR ADDING** rows or columns in input screens may cause the program to crash.
- 3) Parameters used in the model are to be entered directly into the white/blue cells.

NOTE: Although literature values are provided, site-specific hydrogeological, transport, and plume characteristic values will likely provide better results. If literature values are used and there is uncertainty in the value chosen, sensitivity analyses should be conducted to determine the effects of the uncertainty on model predictions.

Data Input Screen:

Step 1: Starting Information

| PARAMETER | SYSTEM UNITS |
|-------------------|--|
| Description | Unit system to perform matrix diffusion calculations in. |
| Units | SI System (meters, etc.) or English Units (feet, etc.). |
| How to Enter Data | Choose the appropriate radio button. |

| PARAMETER | MEDIA TYPE |
|-------------------|--|
| Description | Pick either “ <i>Unconsolidated</i> ” (units comprised of gravel/sand/silt/clay) or “ <i>Fractured Rock/Media</i> ” (units comprised of fractured rock or fractured clay). |
| How to Enter Data | Select radio button. |

Step 2: Model Configuration

| PARAMETER | X-DIRECTION CELL SIZE |
|-------------------|--|
| Units | ft (or m). |
| Description | Finite difference modeling parameter representing the size of each cell in the modeling grid in the x-direction. The minimum cell size value should be greater than zero. |
| Typical Values | 1 – 330 ft (0.3 – 100 m). |
| How to Enter Data | Enter directly. Note that the total number of grid cells (X-direction model size / X-direction cell size) in the X-direction cannot be greater than 2000. |

| PARAMETER | X-DIRECTION MODEL SIZE |
|-------------------|--|
| Units | ft (or m). |
| Description | Finite difference modeling parameter representing the model domain in the x-direction. |
| Typical Values | 1 – 6600 ft (0.3 – 2000 m). |
| Source of Data | Plume maps. |
| How to Enter Data | Enter directly. Note that the total number of grid cells (X-direction model size / X-direction cell size) in the X-direction cannot be greater than 2000. |

DATA ENTRY

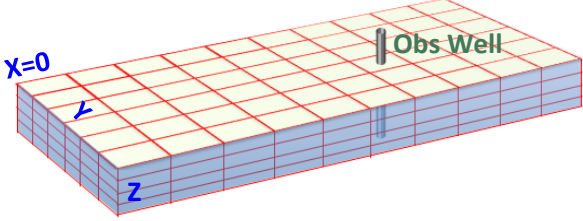
| PARAMETER | Y-DIRECTION CELL SIZE |
|-------------------|--|
| Units | ft (or m). |
| Description | Finite difference modeling parameter representing the size of each cell in the modeling grid in the y-direction. The minimum cell size value should be greater than zero. |
| Typical Values | 1 – 330 ft (0.3 – 100 m). |
| How to Enter Data | Enter directly. Note that the total number of grid cells (Y-direction model size / Y-direction cell size) in the Y-direction cannot be greater than 100. |

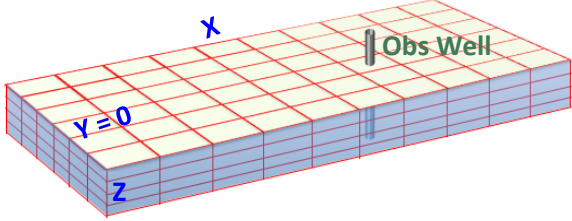
| PARAMETER | Y-DIRECTION MODEL SIZE |
|-------------------|---|
| Units | ft (or m). |
| Description | Finite difference modeling parameter representing the model domain in the y-direction. Note that the model is symmetric around y=0. |
| Typical Values | 10 – 1000 ft (3 – 300 m). |
| Source of Data | Plume maps. |
| How to Enter Data | Enter directly. Note that the total number of grid cells (Y-direction model size / Y-direction cell size) in the Y-direction cannot be greater than 100. |

| PARAMETER | Z-DIRECTION CELL SIZE |
|-------------------|--|
| Units | ft (or m). |
| Description | Finite difference modeling parameter representing the size of each cell in the modeling grid in the z-direction. The minimum cell size value should be greater than zero. (Note that very thin layers, on the centimeter scale, that may be needed to model matrix diffusion in conventional numerical models (e.g., see Rasa <i>et al.</i> , 2011; Chapman <i>et al.</i> , 2012; Sale <i>et al.</i> , 2013 Section 5) are not required for REMChlor-MD as a matrix diffusion specific numerical formulation is built into the tool). |
| Typical Values | 1 – 20 ft (0.3 – 7 m) |
| How to Enter Data | Enter directly. Note that the total number of grid cells (Z-direction model size / Z-direction cell size) in the Z-direction cannot be greater than 50. |

| PARAMETER | Z-DIRECTION MODEL SIZE |
|-------------------|--|
| Units | ft (or m). |
| Description | Finite difference modeling parameter representing the model domain in the z-direction. |
| Typical Values | 1 – 200 ft (0.3 – 60 m). |
| Source of Data | Plume cross-sections. |
| How to Enter Data | Enter directly. Note that the total number of grid cells (Z-direction model size / Z-direction cell size) in the Z-direction cannot be greater than 50. |

DATA ENTRY

| PARAMETER | OBSERVATION WELL LOCATION – X-VALUE |
|-------------------|--|
| Units | ft (or m). |
| Description | <p>X-direction location of the observation well to be used by REMChlor-MD to estimate transmissive zone groundwater concentrations.</p>  <p>The diagram shows a 3D perspective of a rectangular grid representing a model domain. The grid is composed of yellow cells on top and blue cells on the bottom. A vertical axis labeled 'Z' is shown on the left side. A horizontal axis labeled 'X' is shown at the front-left corner, with a blue arrow pointing to the right and the label 'X=0' next to it. A vertical line representing an observation well is shown on the right side of the grid, labeled 'Obs Well' in green text.</p> |
| How to Enter Data | Enter directly. Note that because REMChlor-MD is a grid-based model, the Toolkit will round the well location to the nearest model cell. |

| PARAMETER | OBSERVATION WELL LOCATION – Y-VALUE |
|-------------------|--|
| Units | ft (or m). |
| Description | <p>Y-direction location of the observation well to be used by REMChlor-MD to estimate transmissive zone groundwater concentrations.</p>  <p>The diagram shows a 3D perspective of a rectangular grid representing a model domain. The grid is composed of yellow cells on top and blue cells on the bottom. A vertical axis labeled 'Z' is shown on the left side. A horizontal axis labeled 'Y' is shown at the front-left corner, with a blue arrow pointing to the right and the label 'Y=0' next to it. A vertical axis labeled 'X' is shown at the top center of the grid. A vertical line representing an observation well is shown on the right side of the grid, labeled 'Obs Well' in green text.</p> |
| How to Enter Data | Enter directly. Note that because REMChlor-MD is a grid-based model, the Toolkit will round the well location to the nearest model cell. Use y = 0 to place the well on the plume centerline. |

| PARAMETER | OBSERVATION WELL Z-VALUE TOP OF SCREEN |
|-------------|---|
| Units | ft (or m). |
| Description | <p>Top of screening interval for the observation well to be used by REMChlor-MD to estimate transmissive zone groundwater concentrations. Note that the Toolkit assumes the bottom of the model domain is at Z = 0.</p> |

DATA ENTRY

| | |
|-------------------|--|
| | |
| How to Enter Data | Enter directly. Note that because REMChlor-MD is a grid-based model, the Toolkit will round the well location to the nearest model cell. |

| PARAMETER | OBSERVATION WELL Z-VALUE BOTTOM OF SCREEN |
|-------------------|---|
| Units | ft (or m). |
| Description | <p>Bottom of screening interval for the observation well to be used by REMChlor-MD to estimate transmissive zone groundwater concentrations. Note that the Toolkit assumes the bottom of the model domain is at Z = 0.</p> <div style="text-align: center;"> </div> |
| How to Enter Data | Enter directly. Note that because REMChlor-MD is a grid-based model, the Toolkit will round the well location to the nearest model cell. |

| PARAMETER | STARTING YEAR OF SIMULATION |
|-------------------|--|
| Units | Year (YYYY). |
| Description | <p>Year source loading started.</p> <p>This is estimated from site historical records and, for matrix diffusion analysis, is almost always from the 1950s, 1960s, 1970s, or early 1980s. If the release was over a long period of time, usually it is better to enter the earliest year.</p> |
| How to Enter Data | Enter directly. |

| PARAMETER | ENDING YEAR OF SIMULATION |
|-------------------|--------------------------------------|
| Units | Year (YYYY). |
| Description | Year to end the modeling simulation. |
| How to Enter Data | Enter directly. |

Step 3: Media Characteristics: Unconsolidated Media

| PARAMETER | TRANSMISSIVE ZONE SOIL TYPE |
|-------------------|--|
| Description | Description of the predominate transmissive zone soil (geologic media) type. |
| How to Enter Data | Choose from drop down list or enter directly. |

| PARAMETER | TRANSMISSIVE ZONE HYDRAULIC CONDUCTIVITY |
|-------------------|--|
| Units | cm/sec, ft(or m)/day, ft(or m)/yr. |
| Description | <p>For unconsolidated systems, this is a measure of the permeability of the predominate transmissive soils in the plume (typically sands or gravels). Do not include the permeability of any low-k layers or lenses (flow characteristics of the low-k material is included in the calculation directly based on data you will add in the Matrix Diffusion section).</p> <p>This value is used to estimate the groundwater Darcy velocity and the tortuosity of the unconsolidated transmissive media.</p> |
| Typical Values | <p>Toolkit default values are the geometric means of the ranges below:</p> <p>Gravels: 3×10^{-2} - 3.0 cm/s</p> <p>Coarse Sand: 9×10^{-5} - 6×10^{-1} cm/s</p> <p>Medium Sand: 9×10^{-5} - 5×10^{-2} cm/s</p> <p>Fine Sand: 2×10^{-5} - 2×10^{-2} cm/s</p> <p>Sand: 1×10^{-3} - 1 cm/s</p> <p>(Newell <i>et al.</i>, 1996; Domenico and Schwartz, 1990.)</p> |
| Source of Data | Aquifer tests (e.g., slug test or pumping tests), if available, or by estimates based on literature values of the predominate soil type in the transmissive zone. |
| How to Enter Data | <p>1) Select units and then select the material type, or</p> <p>2) Enter directly. (Note that if the soil type is selected from the drop down list, the Toolkit provides a default value for the parameter.)</p> |

| PARAMETER | TRANSMISSIVE ZONE EFFECTIVE POROSITY |
|----------------|---|
| Units | Unitless. |
| Description | <p>Dimensionless ratio of the volume of voids to the bulk volume of the surface soil column matrix. Note that <i>total porosity</i> is the ratio of all voids (including non-connected voids) to the bulk volume of the aquifer matrix. Differences between total and effective porosity reflect lithologic controls on pore structure. In unconsolidated sediments coarser than silt size, effective porosity can be less than total porosity by 2-5% (e.g., 0.28 vs. 0.30) (Smith and Wheatcraft, 1993).</p> |
| Typical Values | <p>Toolkit default values provided are averages of the ranges below.</p> <p>Gravel: 0.10 - 0.35 Coarse Sand: 0.20 - 0.35</p> <p>Fine Sand: 0.10 - 0.30 Medium Sand: 0.15 - 0.30</p> <p><i>A more recent interpretation based on evaluation of remediation scale tracer tests is that effective (or "mobile") porosity typically falls in the 0.02 to 0.10 range (Payne <i>et al.</i>, 2008). This effect can be included in REMChlor-MD by using a lower volume fraction for the transmissive zone in the heterogeneity</i></p> |

DATA ENTRY

| | |
|-------------------|---|
| | calculator. |
| Source of Data | Typically estimated. Occasionally obtained through physical property testing of site soil samples. One commonly used value for silts and sands is 0.25. The ASTM RBCA Standard (ASTM, 1995) includes a default value of 0.38 (to be used primarily for unconsolidated deposits). A collection of default values is presented in the Geologic Parameter Database included in this manual. |
| How to Enter Data | Enter directly. (Note that if the transmissive zone description is selected from the drop down list, the Toolkit provides a default value for the parameter.) |

| PARAMETER | TRANSMISSIVE ZONE TORTUOSITY |
|-------------------|--|
| Units | Unitless. |
| Description | Tortuosity (τ) represents molecular diffusion in a porous medium. For unconsolidated media, estimations of τ can be obtained using the relationship: $\tau = 0.77K^{0.040}$ Where K is the hydraulic conductivity in meters/second from the value entered above (Carey <i>et al.</i> , 2016). |
| How to Enter Data | 1) Enter directly, or 2) Calculate by pressing the "Default Tortuosity" button. (Note that if the zone description is selected from the drop down list, the Toolkit provides a default value for the parameter.) |

| PARAMETER | LOW-K ZONE SOIL TYPE |
|-------------------|---|
| Description | Description of the predominate low-k zone soil (geologic media) type. |
| How to Enter Data | Choose from drop down list or enter directly. |

| PARAMETER | LOW-K ZONE HYDRAULIC CONDUCTIVITY |
|----------------|--|
| Units | cm/sec, ft(or m)/day, ft(or m)/yr. |
| Description | For unconsolidated systems, this is a measure of the permeability of the predominate low-k soils in the plume (typically silts and clays). This value is used only to estimate the tortuosity of the low-k soils if a tortuosity value is not provided directly. |
| Typical Values | Toolkit default values are the geometric means of the ranges below: <u>Horizontal K</u> Clay: 1×10^{-9} - 4.7×10^{-7} cm/s Silt: 1×10^{-7} - 2×10^{-3} cm/s (Newell <i>et al.</i> , 1996; Freeze and Cherry, 1979; Domenico and Schwartz, 1990.) Note, for vertical hydraulic conductivities, dividing horizontal K by a factor of 3 or less is common for homogenous aquifers while dividing by a factor of 10 or more may be appropriate for heterogeneous aquifers (Freeze and Cherry, 1979; Parker <i>et al.</i> , 2004). |

DATA ENTRY

| | |
|-------------------|--|
| Source of Data | Typically, this value will be estimated based on literature values for a particular soil type (silt, clays), but at some sites measurements of aquitard hydraulic conductivity may be available and therefore can be used. |
| How to Enter Data | 1) Select drop down option for material, or 2) Enter directly. (Note that if the soil type is selected from the drop down list, the Toolkit provides a value for the parameter.) |

| PARAMETER | LOW-k ZONE TOTAL POROSITY |
|-------------------|--|
| Units | Unitless. |
| Description | Dimensionless ratio of the volume of voids to the bulk volume of the surface soil column matrix, but excluding secondary porosity (fractures, solution cavities, etc.). <i>Total porosity</i> is the ratio of all voids (including non-connected voids) to the bulk volume of the aquifer matrix. Effective porosity and any porosity data with secondary porosity information should not be used. |
| Typical Values | Toolkit default values provided are averages of the ranges below: Clay: 0.34 - 0.60 (Payne <i>et al.</i> , 2008, Table 2.3.) Silt: 0.34 - 0.61 (Payne <i>et al.</i> , 2008, Table 2.3.) |
| Source of Data | Typically estimated. Occasionally obtained through physical property testing of site soil samples. |
| How to Enter Data | Enter directly. (Note that if the low-k zone description is selected from the drop down list, the Toolkit provides a default value for the parameter.) |

| PARAMETER | LOW-K ZONE TORTUOSITY |
|-------------------|--|
| Units | Unitless. |
| Description | Tortuosity (τ) represents molecular diffusion in a porous medium. For unconsolidated systems, estimations of τ can be obtained using the relationship: $\tau = 0.77K^{0.040} \quad (1)$ Where K is the hydraulic conductivity in meters/second from the value entered above (Carey <i>et al.</i> , 2016). In the Toolkit, Equation 1 is used to calculate the default tortuosity for all unconsolidated materials. |
| How to Enter Data | 1) Enter directly, or 2) Calculate by pressing the "Default Tortuosity" button. (Note that if the zone description is selected from the drop down list, the Toolkit provides a default value for the parameter.) |

| PARAMETER | TRANSMISSIVE ZONE HYDRAULIC GRADIENT |
|----------------|--|
| Units | ft/ft (or m/m). |
| Description | The slope of the potentiometric surface. In unconfined aquifers, this is equivalent to the slope of the water table. |
| Typical Values | 0.0001 - 0.1 ft/ft (0.0001 - 0.1 m/m). |

DATA ENTRY

| | |
|-------------------|--|
| Source of Data | Calculated by constructing potentiometric surface maps using static water level data from monitoring wells and estimating the slope of the potentiometric surface. |
| How to Enter Data | Enter directly. |

Step 3: Media Characteristics: Fractured Rock/Media

| PARAMETER | HYDROGEOLOGIC SETTING |
|-------------------|---|
| Description | Description of the predominate fractured rock/media matrix (geologic media) type. |
| How to Enter Data | Choose from drop down list or enter directly. |

| PARAMETER | BULK K |
|-------------------|--|
| Units | cm/sec, ft(or m)/day, ft(or m)/yr. |
| Description | For fractured media, this value represents the hydraulic conductivity of the fractured system (fractures only) and assumes that flow in the fractured system follows Darcy's law. |
| Typical Values | <p>Toolkit default values are the geometric means of the ranges below:</p> <p><u>Horizontal K</u></p> <p>Fractured Clay: 1×10^{-9} - 4.7×10^{-7} cm/s Fractured Sandstone: 1×10^{-6} - 1×10^{-2} cm/s Granite: 3×10^{-4} - 5.2×10^{-3} cm/s Limestone/Dolomite: 1×10^{-7} - 6×10^{-4} cm/s Permeable Basalt*: 4×10^{-5} - 2 cm/s Sandstone: 3×10^{-8} - 6×10^{-4} cm/s Shale: 1×10^{-11} - 2×10^{-7} cm/s (Newell <i>et al.</i>, 1996; Freeze and Cherry, 1979; Domenico and Schwartz, 1990; *GSI, 2018.)</p> |
| Source of Data | Typically, this value will be estimated based on literature values for a particular fractured media, but at some sites measurements of aquitard hydraulic conductivity may be available and therefore can be used. |
| How to Enter Data | <ol style="list-style-type: none"> 1) Select drop down option for material, or 2) Enter directly. (Note that if the soil type is selected from the drop down list, the Toolkit provides a value for the parameter.) |

| PARAMETER | FRACTURE POROSITY |
|-------------|--|
| Units | Unitless. |
| Description | Dimensionless ratio of the volume of voids to the bulk volume of the fractures. If there are no small particles such as sand in the fracture, then this value is 1.0). If the fractures are filled with sand, a value of 0.3 is more representative. |

DATA ENTRY

| | |
|-------------------|---|
| Typical Values | Toolkit defaults a value of 1 for all media types. |
| Source of Data | Typically estimated based on the knowledge of if the fractures contain porous media or are free of porous media. |
| How to Enter Data | Enter directly. (Note that if the hydrogeologic setting description is selected from the drop down list, the Toolkit provides a default value for the parameter.) |

| PARAMETER | TRANSMISSIVE ZONE TORTUOSITY |
|-------------------|--|
| Units | Unitless. |
| Description | Tortuosity (τ) represents molecular diffusion in a fracture (not the matrix). For fractured systems, a default tortuosity of 1 is used in the Toolkit. |
| How to Enter Data | 1) Enter directly, or 2) Calculate by pressing the "Default Tortuosity" button. (Note that if the zone description is selected from the drop down list, the Toolkit provides a default value for the parameter.) |

| PARAMETER | MATRIX POROSITY |
|-------------------|--|
| Units | Unitless. |
| Description | Dimensionless ratio of the volume of voids to the bulk volume of the fractured media matrix, but excluding secondary porosity (fractures, solution cavities, etc. |
| Typical Values | Toolkit default values provided are averages of the ranges below: Clay: 0.34 - 0.60 (Payne <i>et al.</i> , 2008, Table 2.3) Limestone/Dolomite: 0 - 0.40 (Domenico and Schwartz, 1990, Table 2.2) Sandstone: 0.05 - 0.15 (Domenico and Schwartz, 1990, Table 2.2) Shale: 0.01 - 0.10 (Domenico and Schwartz, 1990, Table 2.2) Granite: 0.006 (Payne <i>et al.</i> , 2008, Table 2.3) Permeable Basalt: 0.03-0.35 (GSI Environmental, 2018) |
| Source of Data | Typically estimated. Occasionally obtained through physical property testing of site soil samples. |
| How to Enter Data | Enter directly. (Note that if the low-k zone description is selected from the drop down list, the Toolkit provides a default value for the parameter.) |

| PARAMETER | MATRIX TORTUOSITY |
|-------------|---|
| Units | Unitless. |
| Description | Tortuosity (τ) represents molecular diffusion in a porous medium. For unconsolidated systems, estimations of τ can be obtained using the relationship: $\tau = 0.77K^{0.040} \quad (1)$ Where K is the hydraulic conductivity in meters/second from the value entered above (Carey <i>et al.</i> , 2016). For fractured systems, estimations of τ can be obtained using the |

DATA ENTRY

| | |
|-------------------|---|
| | <p>relationship:</p> $\frac{D_e}{D_o} = \tau \cong \phi^p \quad (2)$ <p>Where D_o is the molecular diffusion coefficient in free water, D_e is the effective diffusion coefficient, ϕ is the porosity and p the Apparent Tortuosity Factor Exponent.</p> <p>Depending on the geologic medium, values for p can vary between 0.3 and 5.4 (Charbeneau, 2000; Pankow and Cherry, 1996; Dullien, 1992; Lerman, 1979; and Millington and Quirk, 1961). Note: Some of these references use a diffusion equation based on a different formulation of Fick's Law, where the effective diffusion coefficient is a function of porosity and frequently referred to as D_e'.</p> <p>Typical values for the Apparent Tortuosity Factor Exponent include:</p> <p>Sandstone/Shale: 1 (calculated from Pankow and Cherry (1996) Table 12.2). The apparent tortuosity factor exponent for sandstone/shale will likely be similar or smaller than silt or clay.</p> <p>Granite: 0.55 (calculated from Pankow and Cherry (1996) Table 12.2). The apparent tortuosity factor exponent for granite will likely be smaller than silt or clay.</p> <p>Limestone/Dolomite: 1</p> <p>Basalt: 0.55</p> <p>In the Toolkit, Equation 1 is used to calculate the default tortuosity for fractured clay and Equation 2 used for all other materials.</p> |
| How to Enter Data | <p>1) Enter directly, or</p> <p>2) Calculate by pressing the "Default Tortuosity" button.</p> <p>(Note that if the zone description is selected from the drop down list, the Toolkit provides a default value for the parameter.)</p> |

| PARAMETER | HYDRAULIC GRADIENT |
|-------------------|--|
| Units | ft/ft (or m/m). |
| Description | The slope of the potentiometric surface. In unconfined aquifers, this is equivalent to the slope of the water table. |
| Typical Values | 0.0001 - 0.1 ft/ft (0.0001 - 0.1 m/m). |
| Source of Data | Calculated by constructing potentiometric surface maps using static water level data from monitoring wells and estimating the slope of the potentiometric surface. |
| How to Enter Data | Enter directly. |

Step 4: Matrix Diffusion

REMChlor-MD represents embedded subsurface heterogeneity based on three geologic factors:

1. **Volume fraction** of the transmissive zone material (i.e., fraction of the plume zone containing transmissive soils);
2. **Characteristic maximum matrix diffusion length** (i.e., how far, on average, contaminants can penetrate into low-k lenses or layers); and

DATA ENTRY

3. **Surface area of the transmissive/low-k interfaces** where contaminant mass has moved or will move between transmissive media (such as sand/gravel or fractures) and low-k soils (such as clay lenses and/or clay layers or the matrix in fractured systems) due to matrix diffusion. This is the interfacial surface area in each gridblock that contains embedded low-K zones. For this reason, its magnitude depends on the size of the gridblock.

REMChlor-MD also can account for matrix diffusion into overlying or underlying aquitards.

Press the “Calculate Heterogeneity” button to start the heterogeneity calculator.

| PARAMETER | UNCONSOLIDATED: STEP 1 – UPPER AND LOWER AQUITARDS |
|-------------------|---|
| Description | <p>Determination of the presence of matrix diffusion in the upper and lower aquitards.</p> <p>Select one of four options:</p> <ul style="list-style-type: none"> • No Matrix Diffusion into the upper and lower boundaries of the model. • Matrix Diffusion in Underlying Low-k Unit – assumes an underlying low-k unit (≥ 3 ft (1 m) thick) is present at the site, <u>but not</u> a top overlying low-k unit. • Matrix Diffusion in Overlying Low-k Unit – assumes an overlying low-k unit (≥ 3 ft (1 m) thick) is present at the site, <u>but not</u> a bottom underlying low-k unit. • Matrix Diffusion in <u>both</u> Under- and Overlying Low-k Units – assumes both an underlying (≥ 3 ft (1 m) thick) and an overlying (≥ 3 ft (1 m) thick) low-k unit are present at the site. |
| Source of Data | Geologic boring logs, cone penetrometer data, direct push hydraulic testing data, geologic cross sections, sequence stratigraphy information, geophysics, or other hydrogeologic data. |
| How to Enter Data | Select radio button and follow prompts. |

| PARAMETER | UNCONSOLIDATED: STEP 2 – EMBEDDED CONDITIONS |
|-------------------|---|
| Description | <p>Entry of additional data regarding the presence and prevalence of embedded low-k zones layers/lenses in the plume zone.</p> <p>Three options are provided for estimating heterogeneity:</p> <ul style="list-style-type: none"> • A simple method with five options for selecting site conditions, • Based on Site-Specific boring log data, or • Direct entry of the Transmissive Zone Volume Fraction, Average Diffusion Length, and Surface Area of Low-k Interfaces. |
| How to Enter Data | Select radio button and follow prompts. |

DATA ENTRY

| PARAMETER | UNCONSOLIDATED: STEP 2 – EMBEDDED CONDITIONS: SIMPLE METHOD |
|-------------------|--|
| Description | <p>Entry of additional data regarding the presence and prevalence of embedded low-k zones layers/lenses in the plume zone. Note that the top and bottom low-k layers identified in Step 1 should not be counted here, just the embedded layers/lenses.</p> <p>Select one of the following five options:</p> <ul style="list-style-type: none"> • 0% of Plume Thickness is in the Low-k Material - assumes no low-k units are present within the plume. If this option is selected there will be no matrix diffusion inside the plume zone, although there still could be matrix diffusion with overlying or underlying aquitards (from the previous step). • ~20% of Plume Thickness is in the Low-k Material. Assumes one or more low-k units collectively representing ~20% of the plume thickness are present at the site. • ~40% of Plume Thickness is in the Low-k Material. Assumes one or more low-k units collectively representing ~40% of the plume thickness are present at the site. • ~60% of Plume Thickness is in the Low-k Material. Assumes one or more low-k units collectively representing ~60% of the plume thickness are present at the site. • ~80% of Plume Thickness is in the Low-k Material. Assumes one or more low-k units collectively representing ~80% of the plume thickness are present at the site. <p>These data are used by REMChlor-MD to calculate the Transmissive Zone Volume Fraction, Average Diffusion Length, and Surface Area of Low-k Interfaces.</p> |
| Source of Data | Geologic boring logs, cone penetrometer data, direct push hydraulic testing data, geologic cross sections, sequence stratigraphy information, geophysics, or other hydrogeologic data. |
| How to Enter Data | Select radio button and follow prompts. |

| PARAMETER | UNCONSOLIDATED: STEP 3 – EMBEDDED THICKNESS: SIMPLE METHOD |
|-------------------|---|
| Description | <p>If one of the options from the Simple Method is selected in Step 2, you must enter a typical thickness of any embedded low-k units. Entry of the typical vertical thickness of embedded low-k lenses/layers in the plume. Note that the top and bottom low-k layers identified in Step 1 should not be counted here, just the embedded layers/lenses.</p> |
| Source of Data | Geologic boring logs, cone penetrometer data, direct push hydraulic testing data, geologic cross sections, sequence stratigraphy information, geophysics, or other hydrogeologic data. |
| How to Enter Data | Select radio button and follow prompts. |

| PARAMETER | UNCONSOLIDATED: STEP 3 – EMBEDDED THICKNESS: SITE-SPECIFIC BORING LOGS |
|-------------|--|
| Description | <p>If the Use Site-Specific Boring Log Data option is selected in Step 2, the Transmissive Zone Volume Fraction, Average Diffusion Length, and Surface Area of Low-k Interfaces can be estimated based on site specific geologic</p> |

DATA ENTRY

| | |
|-------------------|---|
| | <p>data, most commonly the data in geologic logs.</p> <p>To calculate Site-Specific heterogeneity parameters, find boring logs that are in different parts of the plume.</p> <ol style="list-style-type: none"> 1. Enter the number of boring logs to be used. Data from up to 100 boring logs can be used. 2. On each boring log, determine the top and bottom of the plume. Don't count the top and bottom low-k. Enter the plume top and bottom for each well into the Toolkit. 3. For each well, enter the thickness of each low-k unit within the plume interval (note that the top and bottom low-k layers identified above should not be counted here). Thicknesses for up to 10 low-k units can be entered. <p>The REMChlor-MD interface then processes these data to calculate site specific values for the three key REMChlor-MD heterogeneity parameters used for unconsolidated media sites: 1) Transmissive Zone Volume Fraction, 2) Average Diffusion Length, and 3) Surface Area of Low-k Interfaces.</p> |
| Source of Data | Geologic boring logs, cone penetrometer data, direct push hydraulic testing data, geologic cross sections, sequence stratigraphy information, geophysics, or other hydrogeologic data. |
| How to Enter Data | Enter directly. |

| PARAMETER | UNCONSOLIDATED: STEP 3 – EMBEDDED THICKNESS: MANUAL ENTRY |
|-------------------|---|
| Description | If the Manual Entry option is selected in Step 2, enter values for the three key REMChlor-MD heterogeneity parameters used for unconsolidated media sites: 1) Transmissive Zone Volume Fraction, 2) Average Diffusion Length, and 3) Surface Area of Low-k Interfaces in the gridblocks. Note that the top and bottom low-k layers identified in Step 1 should not be counted here, just the embedded layers/lenses. |
| Source of Data | Geologic boring logs, cone penetrometer data, direct push hydraulic testing data, geologic cross sections, sequence stratigraphy information, geophysics, or other hydrogeologic data. |
| How to Enter Data | Select radio button and follow prompts. |

| PARAMETER | FRACTURED ROCK/MEDIA: STEP 1 – UPPER AND LOWER AQUITARDS |
|-------------|--|
| Description | <p>Determination of the presence of matrix diffusion in the unfractured upper and lower aquitards.</p> <p>Select one of four options:</p> <ul style="list-style-type: none"> • No Matrix Diffusion into the upper and lower boundaries of the model. This option is appropriate if the fracture spacing is large. • Matrix Diffusion in Unfractured Underlying Low-k Unit – assumes an underlying low-k unit (≥ 3 ft (1 m) thick) is present at the site, <u>but not</u> a top overlying low-k unit. • Matrix Diffusion in Unfractured Overlying Low-k Unit – assumes an overlying low-k unit (≥ 3 ft (1 m) thick) is present at the site, <u>but not</u> a bottom underlying low-k unit. • Matrix Diffusion in <u>both</u> Under- and Overlying Low-k Units – assumes both an underlying (≥ 3 ft (1 m) thick) and an overlying (\geq |

DATA ENTRY

| | |
|-------------------|---|
| | 3 ft (1 m) thick) low-k unit are present at the site. |
| Source of Data | Fractured rock: geologic boring logs, geologic cross sections, geophysics, or other hydrogeologic data. Fractured clay: cone penetrometer data, direct push hydraulic testing data, or other data may be useful. |
| How to Enter Data | Select radio button and follow prompts. |

| PARAMETER | FRACTURED ROCK/MEDIA: STEP 2 – TYPICAL DISTANCE BETWEEN PARALLEL FRACTURES |
|-------------------|---|
| Description | Typical distance between parallel fractures (they can be in the X-, Y-, or any direction). REMChlor-MD is not able to model fractures in two directions at the same location, but will provide a reasonable simulation of the style of matrix diffusion in a fractured media. |
| Typical Values | 1 to 30 (ft) (0.3 to 10 m) |
| Source of Data | Fractured rock/media site characterization tools (borehole flowmeters, borehole geophysics, geologic logs, evaluation of surface expression of fractures, geophysics, borehole video, etc.) |
| How to Enter Data | Enter directly. |

| PARAMETER | FRACTURED ROCK/MEDIA: STEP 2 – TYPICAL THICKNESS OF APERTURE/FRACTURE |
|-------------------|---|
| Description | Typical thickness of the aperture/fracture best representative of the site being modeled. |
| Typical Values | 3×10^{-6} to 0.3 (ft) (1×10^{-6} to 0.1 m) |
| Source of Data | Fractured rock/media site characterization tools (borehole flowmeters, borehole geophysics, geologic logs, evaluation of surface expression of fractures, geophysics, borehole video, etc.) |
| How to Enter Data | Enter directly. |

Step 5: Contaminants and Source Term

| PARAMETER | CONSTITUENT |
|-------------------|---|
| Description | Constituent(s) of interest. |
| How to Enter Data | Enter directly or choose from drop down list. Component 1 is the parent compound and is the component released from the source zone. Component 2 is the decay product of the parent compound and Component 3 is the decay product of Component 2. Component 4 is the decay product of Component 3 and is assumed to decay into a harmless specie. |

DATA ENTRY

| PARAMETER | INITIAL SOURCE CONCENTRATION |
|-------------------|--|
| Units | ug/L or mg/L or kg/m ³ . |
| Description | Initial source zone concentration when the simulation starts. |
| Typical Values | 0.0001 – 20,000 mg/L. |
| Source of Data | Estimated using 1) historical knowledge of site; 2) estimates of equilibrium concentrations caused by historical DNAPL sources, 3) if no other data, use the highest concentration from the entire historical monitoring well record; or 4) application of the ESTCP Source History Tool (Farhat <i>et al.</i> , 2013; ESTCP project ER-201032). |
| How to Enter Data | Enter directly. Component 1 is the parent compound and a required entry. Component 2 (the decay product of the parent compound), Component 3 (the decay product of Component 2), and Component 4 (the decay product of Component 3) are optional entries. |

| PARAMETER | SOURCE MASS AT TIME OF RELEASE |
|-------------------|---|
| Units | Kg. |
| Description | Initial source zone contaminant mass(es). |
| Typical Values | 0.1 – 1,000,000 kg. |
| Source of Data | Estimated using 1) historical knowledge of site; or 2) analysis of soil samples and extrapolations to estimate mass released to the subsurface; or 3) best estimate. If unknown use ranges to bound the modeling simulation with REMChlor-MD. |
| How to Enter Data | Enter directly. Component 1 is the parent compound and a required entry. Component 2 (the decay product of the parent compound), Component 3 (the decay product of Component 2), and Component 4 (the decay product of Component 3) are optional entries. |

| PARAMETER | RETARDATION FACTOR IN T-ZONE (TRANSMISSIVE ZONE) |
|----------------|---|
| Units | Unitless. |
| Description | The retardation factor is the ratio of the dissolved plus sorbed constituent mass to the dissolved constituent mass in the aqueous phase in a unit volume of aquifer. It is a function of both transmissive zone soil type and contaminant properties. |
| Typical Values | For transmissive zones, these retardation factors are commonly observed: 1-3 (typical for BTEX) 2-5 (typical for many chlorinated solvents) |
| Source of Data | Usually estimated from soil and chemical data using the following expression: $R = 1 + K_d \cdot \rho_d / n$ where $K_d = K_{oc} \cdot f_{oc}$ where ρ_d = bulk density, n = porosity, K_{oc} = organic carbon-water partition coefficient, K_d = distribution coefficient, and f_{oc} = fraction organic carbon on uncontaminated soil. In some cases, the retardation factor can be estimated by comparing the |

DATA ENTRY

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|-------------------|--|
| | length of a plume affected by adsorption (such as the benzene plume) with the length of plume that is not affected by adsorption (such as chloride). Most plumes do not have both types of constituents, so it is more common to use the estimation technique. (See "fraction organic carbon" below for more information.) |
| How to Enter Data | <p>1) Enter directly, or</p> <p>2) Calculate by pressing the "Calculate R" button and entering values for:</p> <p style="margin-left: 40px;">a) Soil Bulk Density, and</p> <p style="margin-left: 40px;">b) Distribution Coefficient or Fraction Organic Carbon and Organic Carbon Partitioning Coefficient.</p> <p>Component 1 is the parent compound, Component 2 is the decay product of the parent compound, Component 3 is the decay product of Component 2, and Component 4 is the decay product of Component 3.</p> |

| PARAMETER | RETARDATION FACTOR IN LOW-K MEDIA |
|-------------------|--|
| Units | Unitless. |
| Description | The retardation factor is the ratio of the dissolved plus sorbed constituent mass to the dissolved constituent mass in the aqueous phase in a unit volume of aquifer. It is a function of both aquifer and constituent properties. |
| Typical Values | <p>For transmissive zones these retardation factors are commonly observed:</p> <p style="margin-left: 40px;">1-3 (typical for BTEX)</p> <p style="margin-left: 40px;">2-5 (typical for many chlorinated solvents)</p> <p>Some researchers suggest that retardation factors may be higher in low-k zones than transmissive zones. Currently, there are few sites where these values have been determined, however.</p> |
| Source of Data | <p>Usually estimated from soil and chemical data using the following expression:</p> $R = 1 + K_d \cdot \rho_d / n$ <p>where $K_d = K_{oc} \cdot f_{oc}$</p> <p>where ρ_d = bulk density, n = porosity, K_{oc} = organic carbon-water partition coefficient, K_d = distribution coefficient, and f_{oc} = fraction organic carbon on uncontaminated soil.</p> <p>In some cases, the retardation factor can be estimated by comparing the length of a plume affected by adsorption (such as the benzene plume) with the length of plume that is not affected by adsorption (such as chloride). Most plumes do not have both types of constituents, so it is more common to use the estimation technique. (See "fraction organic carbon" below for more information.)</p> |
| How to Enter Data | <p>1) Enter directly, or</p> <p>2) Calculate by pressing the "Calculate R" button and entering values for:</p> <p style="margin-left: 40px;">a) Soil Bulk Density, and</p> <p style="margin-left: 40px;">b) Distribution Coefficient or Fraction Organic Carbon and Organic Carbon Partitioning Coefficient.</p> <p>Component 1 is the parent compound, Component 2 is the decay product of the parent compound, Component 3 is the decay product of Component 2, and Component 4 is the decay product of Component 3.</p> |

DATA ENTRY

| PARAMETER | SOIL BULK DENSITY IN T-ZONE |
|-------------------|---|
| Units | g/mL. |
| Description | Density of the saturated transmissive zone aquifer material (referred to as "soil"), excluding soil moisture. |
| Typical Values | Although this value can be measured in the lab, in most cases estimated values are used. A value of 1.7 g/mL is used frequently. |
| Source of Data | Either from an analysis of soil samples at a geotechnical lab or more commonly, application of estimated values such as 1.7 g/mL. |
| How to Enter Data | Enter directly. |

| PARAMETER | SOIL BULK DENSITY IN LOW-K | | | | | | | | | | | | | | |
|---|--|------------------------------|--------------------|------------------------|---------------------|-------------------------|-----------------------|------------------|--------------------------|---|-------------------------|--------------------------|----------------------------------|------------------------------|----------------------|
| Units | g/mL. | | | | | | | | | | | | | | |
| Description | Density of the saturated low k zone (referred to as "soil"), excluding soil moisture. | | | | | | | | | | | | | | |
| Typical Values | <p>Although this value can be measured in the lab, in most cases estimated values are used. A value of 1.7 g/mL is used frequently for unconsolidated media. Representative values for specific geologic media are shown below (Lovanh <i>et al.</i>, 2000; derived from Domenico and Schwartz, 1990):</p> <table style="width: 100%; border: none;"> <tr> <td style="width: 50%;">Clay: ranges from 1.0 to 2.4</td> <td style="width: 50%;">Loess: 0.75 to 1.6</td> </tr> <tr> <td>Sandstone: 1.6 to 2.68</td> <td>Shale: 1.54 to 3.17</td> </tr> <tr> <td>Limestone: 1.74 to 2.79</td> <td>Granite: 2.24 to 2.46</td> </tr> <tr> <td>Basalt: 2 to 2.7</td> <td>Medium Sand: 1.34 – 1.81</td> </tr> </table> <p>Koerner (1984) reports these values for unit weight for saturated soils (note, no dry bulk density values are reported for these materials):</p> <table style="width: 100%; border: none;"> <tr> <td style="width: 50%;">Glacial till, very mixed grain: 2.32 g/mL</td> <td style="width: 50%;">Soft glacial clay: 1.77</td> </tr> <tr> <td>Stiff glacial clay: 2.07</td> <td>Soft slightly organic clay: 1.58</td> </tr> <tr> <td>Soft very organic clay: 1.43</td> <td>Soft bentonite: 1.27</td> </tr> </table> | Clay: ranges from 1.0 to 2.4 | Loess: 0.75 to 1.6 | Sandstone: 1.6 to 2.68 | Shale: 1.54 to 3.17 | Limestone: 1.74 to 2.79 | Granite: 2.24 to 2.46 | Basalt: 2 to 2.7 | Medium Sand: 1.34 – 1.81 | Glacial till, very mixed grain: 2.32 g/mL | Soft glacial clay: 1.77 | Stiff glacial clay: 2.07 | Soft slightly organic clay: 1.58 | Soft very organic clay: 1.43 | Soft bentonite: 1.27 |
| Clay: ranges from 1.0 to 2.4 | Loess: 0.75 to 1.6 | | | | | | | | | | | | | | |
| Sandstone: 1.6 to 2.68 | Shale: 1.54 to 3.17 | | | | | | | | | | | | | | |
| Limestone: 1.74 to 2.79 | Granite: 2.24 to 2.46 | | | | | | | | | | | | | | |
| Basalt: 2 to 2.7 | Medium Sand: 1.34 – 1.81 | | | | | | | | | | | | | | |
| Glacial till, very mixed grain: 2.32 g/mL | Soft glacial clay: 1.77 | | | | | | | | | | | | | | |
| Stiff glacial clay: 2.07 | Soft slightly organic clay: 1.58 | | | | | | | | | | | | | | |
| Soft very organic clay: 1.43 | Soft bentonite: 1.27 | | | | | | | | | | | | | | |
| Source of Data | Either from an analysis of soil samples at a geotechnical lab or more commonly, application of estimated values such as 1.7 g/mL. | | | | | | | | | | | | | | |
| How to Enter Data | Enter directly. | | | | | | | | | | | | | | |

| PARAMETER | FRACTION ORGANIC CARBON IN T-ZONE |
|----------------|---|
| Units | Unitless (gram per gram). |
| Description | Fraction of the aquifer material comprised of natural organic carbon in uncontaminated areas. More natural organic carbon means higher adsorption of organic constituents on the aquifer matrix. |
| Typical Values | 0.0002 - 0.02 for transmissive zones. |
| Source of Data | The fraction organic carbon value should be measured, if possible, by collecting a sample of aquifer material from an uncontaminated saturated zone and performing a laboratory analysis for transmissive zones (e.g. ASTM Method 2974-87 or equivalent). If unknown, a default value of 0.001 is often used (e.g., ASTM 1995). |

DATA ENTRY

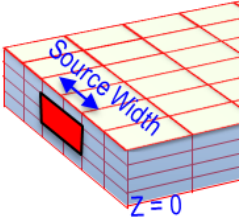
| | |
|-------------------|-----------------|
| How to Enter Data | Enter directly. |
|-------------------|-----------------|

| PARAMETER | FRACTION ORGANIC CARBON IN LOW-K |
|-------------------|--|
| Units | Unitless (gram per gram). |
| Description | Fraction of the aquifer material comprised of natural organic carbon in uncontaminated areas. More natural organic carbon means higher adsorption of organic constituents on the aquifer matrix. |
| Typical Values | <p>Although based on limited data, 0.0002 - 0.10 for low-K zones is a likely range. But some sites may be higher or lower.</p> <p>Examples:</p> <p>At the Moffatt Field site, the f_{oc} of the clay fraction f_{oc} was about 0.0066 (Roberts <i>et al.</i>, 1990).</p> <p>Domenico and Schwartz (1990) report these values: silt (Wildwood Ontario): 0.00102; from Oconee River sediment: Coarse silt: 0.029; Medium silt: 0.02; fine silt; 0.0226.</p> <p>Chapman and Parker (2005) report a f_{oc} of glaciolacustrine aquitard composed of varved silts and clays: 0.0024 to 0.00104 with an average of 0.00054.</p> <p>Adamson (2012) reports $f_{oc} = 0.001$ for a clay layer in Jacksonville Florida and f_{oc} values for silts at the MMR site in Massachusetts ranging from <0.0005 to 0.0022 (median value = 0.0014) for one core using a Leco carbon analyzer; a second core had f_{oc} values < 0.005 for 10 samples and two samples with 0.00067 and 0.00084 (gram per gram). Values for f_{oc} using Walkley-Black wet oxidation method were generally higher by a factor of 2 to 3.</p> <p>Values ranging from 0 to 0.078 have been reported for silts at F.W. Warren site in Wyoming, with a median value of 0.</p> |
| Source of Data | The fraction organic carbon value should be measured, if possible, by collecting a sample of aquifer material from an uncontaminated saturated zone and performing a laboratory analysis (e.g. ASTM Method 2974-87 or equivalent). If unknown, a default value of 0.002 could be used (twice the typical default of 0.001 value used for transmissive systems). |
| How to Enter Data | Enter directly. |

| PARAMETER | ORGANIC CARBON PARTITIONING COEFFICIENT | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|------------------------|---|-----------------------|----------|------|---------|--------------------|---------|-------------------|----------|--------------------|---------|-----------------|---------|--------------------|---------|---------|----------|---------|---------|----------------|---------|------------------------|---------|--------|----------|--------------|----------|--|--|
| Units | mL/g. | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Description | Chemical-specific partition coefficient between soil organic carbon and the aqueous phase. Larger values indicate greater affinity of organic constituents for the organic carbon fraction of soil. This value is chemical specific and can be found in chemical reference books. | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Typical Values | <table style="width: 100%; border: none;"> <tr> <td style="width: 33%;">1,1,1-Trichloroethane</td> <td style="width: 33%;">110 mL/g</td> <td style="width: 33%;">MTBE</td> <td style="width: 33%;">14 mL/g</td> </tr> <tr> <td>1,1-Dichloroethane</td> <td>32 mL/g</td> <td>Tetrachloroethene</td> <td>155 mL/g</td> </tr> <tr> <td>1,1-Dichloroethene</td> <td>65 mL/g</td> <td>Trichloroethene</td> <td>93 mL/g</td> </tr> <tr> <td>1,2-Dichloroethane</td> <td>17 mL/g</td> <td>Toluene</td> <td>140 mL/g</td> </tr> <tr> <td>Benzene</td> <td>66 mL/g</td> <td>Vinyl Chloride</td> <td>11 mL/g</td> </tr> <tr> <td>cis-1,2-Dichloroethene</td> <td>29 mL/g</td> <td>Xylene</td> <td>240 mL/g</td> </tr> <tr> <td>Ethylbenzene</td> <td>204 mL/g</td> <td></td> <td></td> </tr> </table> | 1,1,1-Trichloroethane | 110 mL/g | MTBE | 14 mL/g | 1,1-Dichloroethane | 32 mL/g | Tetrachloroethene | 155 mL/g | 1,1-Dichloroethene | 65 mL/g | Trichloroethene | 93 mL/g | 1,2-Dichloroethane | 17 mL/g | Toluene | 140 mL/g | Benzene | 66 mL/g | Vinyl Chloride | 11 mL/g | cis-1,2-Dichloroethene | 29 mL/g | Xylene | 240 mL/g | Ethylbenzene | 204 mL/g | | |
| 1,1,1-Trichloroethane | 110 mL/g | MTBE | 14 mL/g | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 1,1-Dichloroethane | 32 mL/g | Tetrachloroethene | 155 mL/g | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 1,1-Dichloroethene | 65 mL/g | Trichloroethene | 93 mL/g | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 1,2-Dichloroethane | 17 mL/g | Toluene | 140 mL/g | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Benzene | 66 mL/g | Vinyl Chloride | 11 mL/g | | | | | | | | | | | | | | | | | | | | | | | | | | |
| cis-1,2-Dichloroethene | 29 mL/g | Xylene | 240 mL/g | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Ethylbenzene | 204 mL/g | | | | | | | | | | | | | | | | | | | | | | | | | | | | |

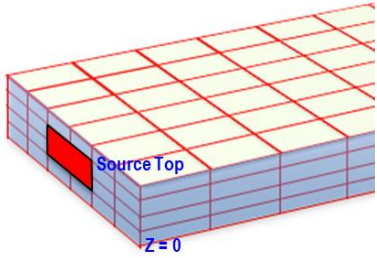
DATA ENTRY

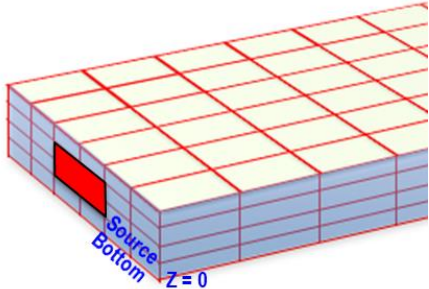
| | |
|-------------------|--|
| | (TRRP, 2008) (Note that there is a wide range of reported values; for example, Mercer and Cohen (1990) report a K_{oc} for benzene of 83 mL/g.) For more information see Pankow and Cherry, 1996 (for solvents) and Wiedemeier <i>et al.</i> , 1999 (variety of constituents). |
| Source of Data | Chemical reference literature such as Pankow and Cherry, 1996 (for solvents); Wiedemeier <i>et al.</i> , 1999 (variety of constituents); or other references with chemical properties. Alternatively, one can use relationships between K_{oc} and solubility or K_{oc} and the octanol-water partition coefficient (K_{ow}) to determine K_{oc} . A collection of values is presented in the Chemical Parameter Database included in this manual. |
| How to Enter Data | Enter directly. (Note that if the constituent is selected from the drop down list, the Toolkit provides a value for the parameter.) |

| PARAMETER | SOURCE WIDTH |
|-------------------|--|
| Units | ft (m). |
| Description | Width of source area perpendicular to groundwater flow. Note that because REMChlor-MD is a grid based model, the Toolkit will round the source width to the nearest model cell. The source width should be at least two (2) times the cell width in the y-direction for best results.  |
| Typical Values | 10 – 1000 ft (3 – 300 m). |
| Source of Data | Estimated using 1) historical knowledge of site; or 2) estimates of historical DNAPL location, and/or 3) plume maps. |
| How to Enter Data | Enter directly. Note that because REMChlor-MD is a grid based model, the Toolkit will round the source width to the nearest model cell. |

| PARAMETER | Z-VALUE FOR TOP OF SOURCE |
|-------------|---|
| Units | ft (m). |
| Description | Z-direction value for defining the top of the vertical location of the source in the model. REMChlor-MD assumes the bottom of the model domain is at $Z = 0$. Note that because REMChlor-MD is a grid based model, the interface will round the source width to the nearest model cell. |

DATA ENTRY

| | |
|-------------------|--|
| |  |
| Source of Data | Estimated using 1) historical knowledge of site; or 2) estimates of historical DNAPL location, and/or 3) plume maps. |
| How to Enter Data | Enter directly. Note that because REMChlor-MD is a grid based model, the interface will round the source width to the nearest model cell. |

| PARAMETER | Z-VALUE FOR BOTTOM OF SOURCE |
|-------------------|---|
| Units | ft (m). |
| Description | Z--direction value for defining the bottom of the vertical location of the source in the model. Note that the Toolkit assumes the bottom of the model domain is at Z = 0. <div style="text-align: center;">  </div> |
| Source of Data | Estimated using 1) historical knowledge of site; or 2) estimates of historical DNAPL location, and/or 3) plume maps. |
| How to Enter Data | Enter directly. Note that because REMChlor-MD is a grid based model, the Toolkit will round the source width to the nearest model cell. |

| PARAMETER | MOLECULAR DIFFUSION COEFFICIENT IN FREE WATER | |
|----------------|--|---|
| Units | cm ² /sec, m ² /sec. | |
| Description | A factor of proportionality representing the amount of substance diffusing across a unit area through a unit concentration gradient in unit time. | |
| Typical Values | 1,1,1-Trichloroethane: 8.8E-06 cm ² /s 1,1-Dichloroethane: 1.1E-05 cm ² /s 1,1-Dichloroethene: 1.0E-05 cm ² /s 1,2-Dichloroethane: 9.9E-06 cm ² /s Benzene: 9.8E-06 cm ² /s cis-1,2-Dichloroethene: 1.1E-05 cm ² /s | MTBE: 9.4E-05 cm ² /s Tetrachloroethene: 8.2E-06 cm ² /s Trichloroethene: 9.1E-06 cm ² /s Toluene: 8.6E-06 cm ² /s Vinyl Chloride: 1.2E-05 cm ² /s Xylene: 8.5E-06 cm ² /s |

DATA ENTRY

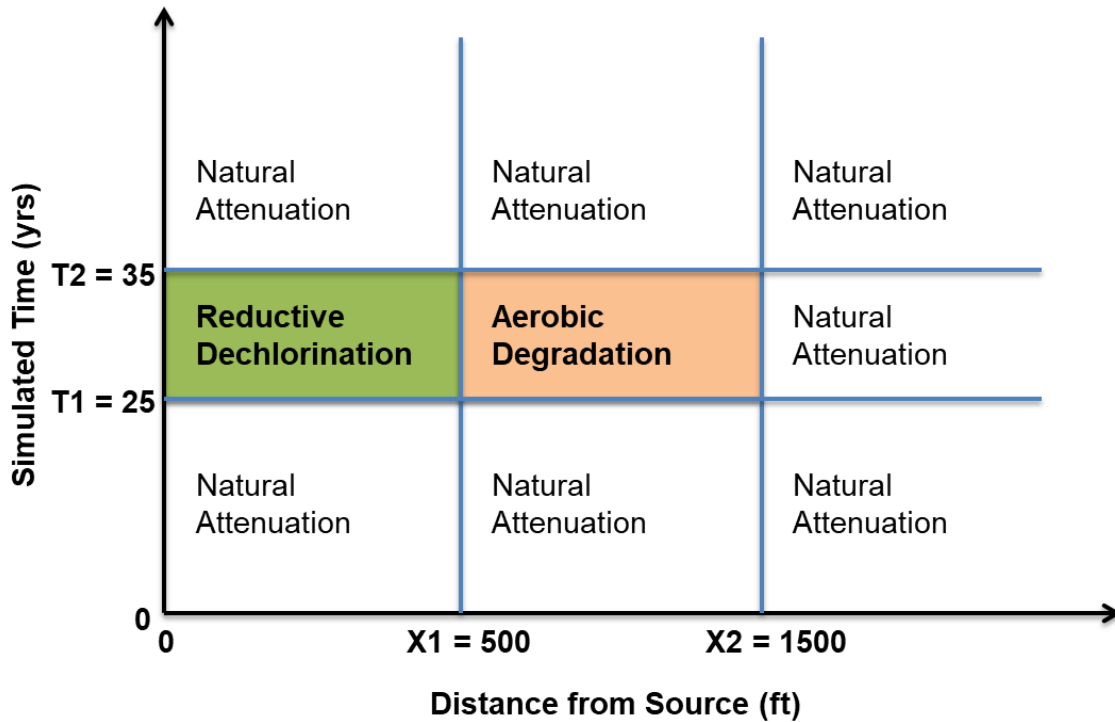
| | |
|-------------------|--|
| | <p>Ethylbenzene: 7.8E-06 cm²/s (TRRP, 2008.)</p> <p>(Note that there is a wide range of reported values, for example, Wiedemeier <i>et al.</i> (1999) report a D_o for benzene of 1.1E-05 cm²/s.) For more information, see Pankow and Cherry, 1996 (for solvents) and Wiedemeier <i>et al.</i>, 1999 (variety of constituents).</p> |
| Source of Data | Chemical reference literature such as Pankow and Cherry, 1996 (for solvents); Wiedemeier <i>et al.</i> , 1999 (variety of constituents); or other references with chemical properties. |
| How to Enter Data | <p>1) Select units, and</p> <p>2) Enter directly. (Note that if the constituent is selected from the drop down list, the Toolkit provides a default value for the parameter.)</p> |

Step 6: Plume Degradation

REMChlor-MD provides nine (9) different plume reaction zones in the transmissive zones (similar to REMChlor (Falta *et al.*, 2007)), and 9 different plume reaction zones in the low-k zone (new to REMChlor-MD). Each of these zones must be entered separately for each component being modeled. Note that the Toolkit assumes that the simulation time starts at zero, when the source release occurs, at the source zone (x = 0 ft).

For example, in the figure below, natural attenuation occurs through the entire length of the plume, downgradient from the source, during the first 25 years since source release. Reductive dechlorination is then simulated from year 25 for 10 years (i.e., from T1 = 25 yrs to T2 = 35 yrs) in the first 500 ft length of the plume. During this same time period, aerobic degradation is simulated in the next 1000 ft segment of the plume (i.e., from X1 = 500 ft to X2 = 1500 ft). Additionally, natural attenuation is assumed for the remaining portion of the plume (i.e., X > 1500 ft). Natural attenuation is also assumed after year 35.

DATA ENTRY



| PARAMETER | TIME PERIOD 1 |
|-------------------|---|
| Units | Year (YYYY) or yrs. |
| Description | <p>Defines the time, T1, when the first plume remediation starts. That is, plume decay rates change from their initial value (which started at T=0 at the source release). Note that this time is unrelated to the time of source remediation.</p> <div style="text-align: center;"> </div> <p>For example, in the figure above, natural attenuation occurs through the entire length of the plume, downgradient from the source, during the first 25 years since source release. Reductive dechlorination is then simulated for 10 years (i.e., from T1 = 25 yrs to T2 = 35 yrs) in the first 500 ft length of the plume. During this same time period, aerobic degradation is simulated in the next 1000 ft segment of the plume (i.e., from X1 = 500 ft to X2 = 1500 ft). Additionally, natural attenuation is assumed for the remaining portion of the plume (i.e., X > 1500 ft). Natural attenuation is also assumed after year 35.</p> |
| How to Enter Data | Enter directly. |

DATA ENTRY

| PARAMETER | TIME PERIOD 2 |
|-------------------|--|
| Units | Year (YYYY) or yrs. |
| Description | <p>Defines the time, T2, when the first plume remediation ends, and the second remediation starts. That is, plume reaction plume decay rates change from their previous value (which started at t=T1). Note that this time is unrelated to the time of source remediation. The third time period occurs after T2.</p> <p>For example, in the figure above, natural attenuation occurs through the</p> <div style="text-align: center;"> </div> <p>entire length of the plume, downgradient from the source, during the first 25 years since source release. Reductive dechlorination is then simulated from year 25 for 10 years (i.e., from T1 = 25 yrs to T2 = 35 yrs) in the first 500 ft length of the plume. During this same time period, aerobic degradation is simulated in the next 1000 ft segment of the plume (i.e., from X1 = 500 ft to X2 = 1500 ft). Additionally, natural attenuation is assumed for the remaining portion of the plume (i.e., X > 1500 ft). Natural attenuation is also assumed after year 35.</p> |
| How to Enter Data | Enter directly. |

| PARAMETER | DISTANCE FROM SOURCE, X1 |
|-------------|---|
| Units | ft (m). |
| Description | <p>Defines the first plume distance (X1) downgradient from the source associated with the first reaction rates, i.e., reaction rates in Zone 1.</p> <div style="text-align: center;"> </div> <p>For example, in the figure above, natural attenuation occurs through the entire length of the plume, downgradient from the source, during the first 25 years since source release. Reductive dechlorination is then simulated from year 25 for 10 years (i.e., from T1 = 25 yrs to T2 = 35 yrs) in the first 500 ft</p> |

DATA ENTRY

| | |
|-------------------|--|
| | length of the plume. During this same time period, aerobic degradation is simulated in the next 1000 ft segment of the plume (i.e., from X1 = 500 ft to X2 = 1500 ft). Additionally, natural attenuation is assumed for the remaining portion of the plume (i.e., X > 1500 ft). Natural attenuation is also assumed after year 35. |
| How to Enter Data | Enter directly. |

| PARAMETER | DISTANCE FROM SOURCE, X2 |
|-------------------|---|
| Units | ft (m). |
| Description | <p>Defines the second plume distance (X2) associated with the second reaction rates, i.e., reaction rates in Zone 2. The third zone occurs beyond X2.</p> <div style="text-align: center;"> </div> <p>For example, in the figure above, natural attenuation occurs through the entire length of the plume, downgradient from the source, during the first 25 years since source release. Reductive dechlorination is then simulated from year 25 for 10 years (i.e., from T1 = 25 yrs to T2 = 35 yrs) in the first 500 ft length of the plume. During this same time period, aerobic degradation is simulated in the next 1000 ft segment of the plume (i.e., from X1 = 500 ft to X2 = 1500 ft). Additionally, natural attenuation is assumed for the remaining portion of the plume (i.e., X > 1500 ft). Natural attenuation is also assumed after year 35.</p> |
| How to Enter Data | Enter directly. |

| PARAMETER | MICROBIAL YIELDS |
|-------------|---|
| Units | Unitless. |
| Description | <p>Mass of progeny created by first order decay of one unit of the parent component. Typically, for reductive dechlorination this would be the molecular weight of the progeny divided by the molecular weight of the parent compound. If a component decays without producing any important progeny, then the yield coefficient from this component would be zero.</p> <p>Yield 2 From 1 = Mass of component 2 created by first order decay of one unit of mass of component 1. Typically, for reductive dechlorination, this would be the molecular weight of component 2 divided by the molecular weight of component 1. If component 1 decays without producing any important daughter products, this yield coefficient would be zero.</p> <p>Yield 3 From 2 = Mass of component 3 created by first order decay of component 2. Typically, for reductive dechlorination, this would be the molecular weight of component 3 divided by the molecular weight of</p> |

DATA ENTRY

| | |
|-------------------|---|
| | <p>component 2. If component 2 decays without producing any important daughter products, this yield coefficient would be zero.</p> <p>Yield 4 From 3 = Mass of component 4 created by first order decay of component 3. Typically, for reductive dechlorination, this would be the molecular weight of component 4 divided by the molecular weight of component 3. If component 3 decays without producing any important daughter products, this yield coefficient would be zero.</p> |
| Typical Values | <p>The REMChlor-MD interface provides default values based on PCE biodegradation of:</p> <p>Yield 2 from 1 = 0.795 (in both the transmissive and low-k zones)</p> <p>Yield 3 from 2 = 0.737 (in both the transmissive and low-k zones)</p> <p>Yield 4 from 3 = 0.64 (in both the transmissive and low-k zones)</p> |
| How to Enter Data | Use the "Enter Custom Microbial Terms" button to overwrite the default values. |

| PARAMETER | PLUME DECAY RATE |
|----------------|---|
| Units | 1/yr. |
| Description | <p>REMChlor-MD provides 9 different plume reaction zones in the transmissive zones and 9 different plume reaction zones in the low-k zone. Each of these zones must be entered separately for each component being modeled. Note that the Toolkit assumes that the simulation time starts at zero, when the DNAPL spill occurs, at the source zone ($x = 0$ ft).</p> <p>Component 1 is the parent compound and is the component released from the source zone. Component 2 is the decay product of the parent compound and Component 3 is the decay product of Component 2. Component 4 is the decay product of Component 3 and is assumed to decay into a harmless specie.</p> <div style="text-align: center;"> </div> <p>For example, in the figure above, natural attenuation occurs through the entire length of the plume, downgradient from the source, during the first 25 years since source release. Reductive dechlorination is then simulated from year 25 for 10 years (i.e., from $T_1 = 25$ yrs to $T_2 = 35$ yrs) in the first 500 ft length of the plume. During this same time period, aerobic degradation is simulated in the next 1000 ft segment of the plume (i.e., from $X_1 = 500$ ft to $X_2 = 1500$ ft). Additionally, natural attenuation is assumed for the remaining portion of the plume (i.e., $X > 1500$ ft). Natural attenuation is also assumed after year 35.</p> |
| Typical Values | BIOCHLOR Database (Aziz <i>et al.</i> , 2000). |

DATA ENTRY

| | Rate Constants (1/yr) | | | | | | |
|------|-----------------------|-----------------|--------|-----------------|---------|------|----|
| | Minimum | 25th Percentile | Median | 75th Percentile | Maximum | Mean | n |
| PCE | 0.8 | -- | 1.1 | -- | 2.4 | 1.4 | 3 |
| TCE | 0.3 | 0.5 | 1.2 | 2.4 | 3.2 | 1.5 | 10 |
| cDCE | 0.1 | 0.7 | 1.2 | 2.2 | 20.9 | 3.5 | 9 |
| VC | 0.4 | 0.6 | 1.7 | 4.9 | 12.2 | 3.6 | 7 |
| TCA | 1.6 | -- | 2.4 | -- | 3.2 | 2.4 | 2 |
| DCA | 0.2 | -- | 0.3 | -- | 1.2 | 0.5 | 3 |

-- : Insufficient data to calculate

Other compilations of plume biodegradation rate data can be found in Aronson and Howard, 1997; Suarez and Rifai, 1999.

| | |
|-------------------|---|
| Source of Data | See Newell <i>et al.</i> , 2002 for a discussion on methods to calculate biodegradation rates. Do not use concentration vs. time rates from individual wells. At most sites, the biodegradation rate will be the key calibration parameter and the biodegradation rates will be adjusted so the predicted groundwater concentrations match the measured groundwater concentrations of the key constituents. |
| How to Enter Data | Select component and enter directly. |

Step 7: Plume Transport

| PARAMETER | LONGITUDINAL DISPERSIVITY |
|----------------|--|
| Units | ft (m). |
| Description | <p>Dispersion refers to the process whereby a dissolved solvent will be spatially distributed because of mechanical mixing and chemical diffusion in the aquifer. These processes develop the "plume" shape that is the spatial distribution of the dissolved solvent mass in the aquifer.</p> <p>Selection of dispersivity values is an arduous process, given the impracticability of measuring dispersion in the field and changing interpretations about the validity of the dispersion model. However, simple estimation techniques based on the length of the plume or distance to the measurement point ("scale") are available from a compilation of field test data.</p> <p>REMChlor-MD uses a finite difference upstream weighting method to calculate the advective flux. This method results in a numerical dispersion that is equivalent to the dispersion that would result from a longitudinal dispersivity of (x-direction cell size)/2. Dispersivity values less than this are ignored in the model. If dispersivity values larger than this are used, the numerical dispersivity is subtracted from the value entered. This approach gives a better match with exact analytical solutions.</p> |
| Typical Values | <p>Conventional practice suggested estimating dispersion based on the expected length (L) of the plume:</p> <p>Longitudinal Dispersivity = 0.1 * L (Pickens and Grisak, 1981.)</p> <p>Or the Xu and Eckstein, 1995, relationship shown as the curved line below:</p> |

DATA ENTRY

| | |
|-------------------|--|
| | <p>(Note a newer interpretation of dispersion (Payne <i>et al.</i>, 2008) suggests that dispersion is a very weak process and that much lower values should be used.)</p> |
| Source of Data | Typically estimated using empirical relationships. |
| How to Enter Data | <ol style="list-style-type: none"> 1) Enter directly, or 2) Calculate by pressing the “Dispersivity Calculator” button and entering values for the plume length. |

| PARAMETER | TRANSVERSE DISPERSIVITY |
|-------------------|---|
| Units | ft (m). |
| Description | <p>Dispersion refers to the process whereby a dissolved solvent will be spatially distributed because of mechanical mixing and chemical diffusion in the aquifer. These processes develop the “plume” shape that is the spatial distribution of the dissolved solvent mass in the aquifer.</p> <p>Selection of dispersivity values is an arduous process, given the impracticability of measuring dispersion in the field and changing interpretations about the validity of the dispersion model. However, simple estimation techniques based on the length of the plume or distance to the measurement point (“scale”) are available from a compilation of field test data.</p> |
| Typical Values | <p>One commonly used value is the ratio of α_t : $\alpha_x = 0.10$.</p> <p>Another commonly used relationship is $0.33 \times \alpha_x$ (Aziz <i>et al.</i>, 1999.)</p> |
| Source of Data | Typically estimated using empirical relationships. |
| How to Enter Data | <ol style="list-style-type: none"> 1) Enter directly, or 2) Calculate by pressing the “Dispersivity Calculator” button and entering values for the plume length. |

DATA ENTRY

| PARAMETER | VERTICAL DISPERSIVITY |
|-------------------|---|
| Units | ft (m). |
| Description | <p>Dispersion refers to the process whereby a dissolved solvent will be spatially distributed because of mechanical mixing and chemical diffusion in the aquifer. These processes develop the “plume” shape that is the spatial distribution of the dissolved solvent mass in the aquifer.</p> <p>Selection of dispersivity values is an arduous process, given the impracticability of measuring dispersion in the field and changing interpretations about the validity of the dispersion model. However, simple estimation techniques based on the length of the plume or distance to the measurement point (“scale”) are available from a compilation of field test data.</p> |
| Typical Values | <p>One commonly used value is the ratio of $\alpha_y : \alpha_x = 0.05$</p> <p>Other commonly used relationships range from $0.025 \alpha_x$ to $0.1 \alpha_x$ (Aziz <i>et al.</i>, 1999.)</p> |
| Source of Data | Typically estimated using empirical relationships. |
| How to Enter Data | <p>1) Enter directly, or</p> <p>2) Calculate by pressing the “Dispersivity Calculator” button and entering values for the plume length.</p> |

Step 8: Source Zone Remediation

| PARAMETER | PERCENT SOURCE MASS REMOVED BY REMEDIATION |
|----------------|--|
| Units | Percent. |
| Description | Percent of source mass removed by source remediation activities. |
| Typical Values | 50% to 100%. |
| Source of Data | <p>Personal knowledge, vendor information, data from the scientific literature, or performance data from multiple site databases. For example, ESTCP’s “Development of an Expanded, High-Reliability Cost and Performance Database for In Situ Remediation Technologies” (McGuire <i>et al.</i>, 2016,</p> <div data-bbox="597 1346 1344 1900" data-label="Figure"> <p>Remediation Performance: Parent CVOC</p> <p>Legend:</p> <ul style="list-style-type: none"> Bioremediation (n=117) Chemical Oxidation (n=70) Thermal Treatment (n=23) Chemical Reduction (n=21) Surfactant (n=4) <p>Y-axis: Max Concentration After Treatment (mg/L)</p> <p>X-axis: Max Concentration Before Treatment (mg/L)</p> <p>Annotations: No Change, 1 OoM Reduction, 2 OoM Reduction, 3 OoM Reduction, 4 OoM Reduction, 5 OoM Reduction, MCL</p> </div> |

DATA ENTRY

| | |
|-------------------|--|
| | ESTCP Project ER-201120) shows results from 235 in-situ chlorinated solvent sites (see graph below). Other sources of remediation performance data include Stroo <i>et al.</i> , 2012 and ITRC, 2011. |
| How to Enter Data | Enter directly. |

| PARAMETER | REMEDATION STARTED IN YEAR |
|-------------------|---|
| Units | Year (YYYY) or yrs. |
| Description | Time when source remediation starts. Note that the Toolkit assumes that the simulation time starts at zero, when the source release occurs. |
| Source of Data | Site history or remediation plans. |
| How to Enter Data | Enter directly. |

| PARAMETER | REMEDATION ENDED IN YEAR |
|-------------------|---|
| Units | Year (YYYY) or yrs. |
| Description | Time when source remediation ends. Note that the Toolkit assumes that the simulation time starts at zero, when the source release occurs. |
| Source of Data | Site history or remediation plans. |
| How to Enter Data | Enter directly. |

| PARAMETER | MASS-FLUX/REMAINING-MASS TERM (GAMMA, Γ) |
|----------------|---|
| Units | Unitless. |
| Description | <p>Relationship between source concentrations and the change in contaminant mass over time (Rao <i>et al.</i>, 2001; Rao and Jawitz, 2003; Parker and Park, 2004; Zhu and Sykes, 2004; Falta <i>et al.</i>, 2005; Falta <i>et al.</i>, 2007):</p> $\frac{C}{C_o} = \left(\frac{M}{M_o}\right)^\Gamma$ <p>Where C_o is the initial source zone concentration, C is the time-dependent source concentration, M_o is the initial source zone mass, and M is the time-dependent source mass.</p> <p>A Γ of zero represents a source that is constant over time until the source is depleted (i.e., the “step-function” model). An exponentially decaying source will result in a value of one. Many sites will have a Γ between 0.5 and 2, with lower values typical of younger sites and larger values reflective of older sites (Falta, <i>et al.</i>, 2007).</p> |
| Typical Values | <p>Step-function source: 0</p> <p>Exponential decay: 1</p> <p>Younger sites: <1</p> <p>Older sites: >1</p> <p>(From Falta, <i>et al.</i>, 2007).</p> |

DATA ENTRY

| | |
|-------------------|--------------------|
| Source of Data | Typically assumed. |
| How to Enter Data | Enter directly. |

| PARAMETER | NATURAL SOURCE DECAY RATE |
|-------------------|--|
| Units | 1/yr. |
| Description | <p>Source decay rate constant due to processes other than flushing, such as degradation in the source zone or radioactive decay. There are no studies that break out this term separately, but there are ways to approximate it. This term will basically degrade the entire source mass (which at actual field sites would include dissolved, sorbed, and DNAPL mass in both transmissive and low-k zones) and apply the first order decay solution.</p> <p>Some studies have measured the point decay rate (or source decay rate) by measuring the first order decay rate in groundwater concentration vs. time data from wells in the source zone (e.g., Newell <i>et al.</i>, 2006). However, the first order decay rate from these studies includes both degradation and flushing, while REMChlor-MD requires only the degradation rate on the mass in the source zone.</p> <p>Options for users are to: 1) set this term as zero to make a conservative assumption of how the source will age over time; 2) perform Natural Source Zone Depletion (NSZD) studies to determine the source attenuation rate. Option 1 is the most common approach, but the other approaches are valid if a user understands the nature of the natural source decay term and wants a more accurate estimate of the source life cycle.</p> |
| Typical Values | Typically set to zero unless NSZD data are available where the contribution from flushing can be removed to leave a first order decay rate that only reflects source zone biodegradation. If the source is radioactive, this would be the natural decay rate of the radionuclide. |
| Source of Data | For a conservative approach, assume this term is zero. In the future, Natural Source Zone Depletion studies designed for chlorinated solvent sites may provide the required input data for this parameter (see the <i>Natural Attenuation of Chlorinated Solvent Source Zone</i> chapter in Newell <i>et al.</i> , 2014). |
| How to Enter Data | Enter directly. |

Step 9: Modeling Parameters

| PARAMETER | TIMESTEP SIZE |
|-------------------|--|
| Units | yr. |
| Description | Finite difference modeling parameter. |
| Typical Values | 0.01 to 1 yr. |
| Source of Data | A rule of thumb is to make sure the timestep size is smaller than: (X-Direction cell size) ÷ (groundwater Darcy velocity) |
| How to Enter Data | Enter directly. |

DATA ENTRY

| PARAMETER | MAXIMUM NUMBER OF ITERATIONS |
|-------------------|--|
| Units | Unitless. |
| Description | Finite difference modeling parameter. The maximum number of Gauss Siedell iterations to prevent an endless convergence loop. |
| Typical Values | 100-500. |
| Source of Data | Trial and error. If the simulation doesn't converge, sometimes it can help to increase the number of iterations (but not often). |
| How to Enter Data | Enter directly. |

| PARAMETER | CONVERGENCE TOLERANCE |
|-------------------|---|
| Units | ug/L or mg/L or kg/m ³ . |
| Description | Finite difference modeling parameter. Convergence tolerance during the Gauss Siedell iteration. |
| Typical Values | Typically, 5 - 8 orders of magnitude lower than the source concentration. |
| Source of Data | Take the (INITIAL SOURCE CONCENTRATION) and divide by 10,000,000. |
| How to Enter Data | Enter directly. |

| PARAMETER | SEE RESULTS EVERY |
|-------------------|---|
| Units | yrs. |
| Description | Time interval over which to plot results. |
| How to Enter Data | Enter directly. |

Input Screen Option Buttons

| PARAMETER | NEXT STEP: SHOW GRAPH |
|-------------|---|
| Description | Proceeds to the results of the modeling analysis. |

| PARAMETER | SHOW PREVIOUS DATA |
|-------------|---|
| Description | Shows the output for previously run analysis. |

| PARAMETER | RETURN TO MAIN SCREEN |
|-------------|---|
| Description | Returns to the REMChlor-MD Main Screen. |

DATA ENTRY

| PARAMETER | NEW SITE/CLEAR DATA |
|-------------|---|
| Description | Clears ALL data in the Toolkit memory banks. Use this button to start a new project. |

| PARAMETER | SAVE/EXPORT DATA |
|-------------|--|
| Description | Saves all model data. DO NOT ADD ANY EXTENSIONS TO FILE NAME WHEN SAVING. |

| PARAMETER | PASTE EXAMPLE |
|-------------|--|
| Description | Clears ALL data in the Toolkit memory banks and pastes an example dataset. The example dataset used in REMChlor-MD is obtained from Tutorial 7 of the original REMChlor model. |

| PARAMETER | LOAD DATA |
|-------------|---|
| Description | Loads data files saved through the Toolkit. DO NOT EDIT ANY TOOLKIT FILES. Editing files may cause the Toolkit to crash. |

REMChlor-MD Results

| PARAMETER | CONCENTRATION IN T-ZONE VS. DISTANCE IN X-DIRECTION |
|-------------|--|
| Description | <p>Concentration in the transmissive zone vs. distance in the x-direction. The user may scroll down the various "Time", "Y", and "Z" values in the boxes to the left of the chart to see the output at a particular time and location. Additionally, graphs for individual components may be turned on and off using the check boxes under "Select Component". The "Total" option displays the sum of all the individual components.</p> <p>The user may use the <i>Log</i> \leftrightarrow <i>Linear</i> button to see the results on a semi-log plot.</p> |

| PARAMETER | CONCENTRATION IN T-ZONE VS. DISTANCE FROM BOTTOM OF MODEL |
|-------------|--|
| Description | <p>Concentration in the transmissive zone vs. distance from the bottom of the model. The user may scroll down the various "Time", "X", and "Y" values in the boxes to the left of the chart to see the output at a particular time and location. Additionally, graphs for individual components may be turned on and off using the check boxes under "Select Component". The "Total" option displays the sum of all the individual components.</p> <p>Note that if only one "Z" cell is modeled, then the output will be in terms of a single point for each component rather than a line.</p> <p>The user may use the <i>Log</i> \leftrightarrow <i>Linear</i> button to see the results on a semi-log plot.</p> |

| PARAMETER | CONCENTRATION IN T-ZONE VS. TIME |
|-------------|---|
| Description | <p>Concentration in the transmissive zone vs. the simulated time. The user may scroll down the various "X", "Y", and "Z" values in the boxes to the left of the chart to see the output at a particular location. Additionally, graphs for individual components may be turned on and off using the check boxes under "Select Component". The "Total" option displays the sum of all the individual components.</p> <p>The user may use the <i>Log</i> \leftrightarrow <i>Linear</i> button to see the results on a semi-log plot.</p> |

| PARAMETER | CONCENTRATION VS. TIME IN OBSERVATION WELL |
|-------------|--|
| Description | <p>Concentration vs. the simulated time in the observation well specified on the input screen. Graphs for individual components may be turned on and off using the check boxes under "Select Component". The "Total" option displays the sum of all the individual components.</p> <p>The user may use the <i>Log</i> \leftrightarrow <i>Linear</i> button to see the results on a semi-log plot.</p> |

REMCHLOR - MD RESULTS

| PARAMETER | MASS DISCHARGE VS. TIME IN T-ZONE |
|-------------|--|
| Description | <p>Mass discharge vs. time in the transmissive zone. The user may scroll down the various "X" values in the box to the left of the chart to see the output at a particular location. Additionally, graphs for individual components may be turned on and off using the check boxes under "Select Component". The "Total" option displays the sum of all the individual components.</p> <p>The user may use the <i>Log</i> \leftrightarrow <i>Linear</i> button to see the results on a semi-log plot.</p> |

| PARAMETER | MASS VS. TIME IN T-ZONE |
|-------------|--|
| Description | <p>Mass vs. time in the transmissive zone. Graphs for individual components may be turned on and off using the check boxes under "Select Component". The "Total" option displays the sum of all the individual components.</p> <p>The user may use the <i>Log</i> \leftrightarrow <i>Linear</i> button to see the results on a semi-log plot.</p> |

| PARAMETER | MASS VS. TIME IN LOW-K ZONE |
|-------------|---|
| Description | <p>Mass vs. time in the low-k zone. Graphs for individual components may be turned on and off using the check boxes under "Select Component". The "Total" option displays the sum of all the individual components.</p> <p>The user may use the <i>Log</i> \leftrightarrow <i>Linear</i> button to see the results on a semi-log plot.</p> |

| PARAMETER | CALCULATE T-ZONE MASS DISCHARGE |
|-------------|--|
| Description | <p>The user may calculate the mass discharge at any X and Time by entering the desired inputs in the white cells to the right of the chart. Note that because the Toolkit is a grid based model, the user provided inputs are rounded down to the closest X and Timestep in the model.</p> |

| PARAMETER | CALCULATE MASS |
|-------------|---|
| Description | <p>The user may calculate the mass at any Time in both the low-k and transmissive zones by entering the desired input in the white cell to the right of the chart. Note that because the Toolkit is a grid based model, the user provided input is rounded down to the closest Timestep in the model.</p> |

Option Buttons

| PARAMETER | NEXT STEP: SAVE/EXPORT DATA |
|-------------|---|
| Description | <p>Saves all model data. DO NOT ADD ANY EXTENSIONS TO FILE NAME WHEN SAVING.</p> |

REMCHLOR-MD RESULTS

| PARAMETER | RETURN TO INPUT SCREEN |
|-------------|--|
| Description | Returns to the REMChlor-MD Input Screen. |

| PARAMETER | RETURN TO MAIN SCREEN |
|-------------|---|
| Description | Returns to the REMChlor-MD Main Screen. |

REMChlor-MD Output Files

| PARAMETER | REMCHLOR-MD OUTPUT FILES |
|-------------|---|
| Description | <p>REMChlor-MD outputs text files created by the FORTRAN model code may be viewed externally. The files are generated in the same folder as the REMChlor-MD software. If a simulation is saved by the User, all output files associated with that simulation are moved to the location selected by the User. Output files include:</p> <ul style="list-style-type: none"> • Discharge.out – mass discharge output. Data is output as: <ul style="list-style-type: none"> ○ Time (yrs), X-direction location (m), ○ Mass discharge for component 1 (kg/yr), ○ Mass discharge for component 2 (kg/yr), ○ Mass discharge for component 3 (kg/yr), and ○ Mass discharge for component 4 (kg/yr). • Obs_well.out – observation well output. Data is output as: <ul style="list-style-type: none"> ○ Time (yrs), ○ Concentration of component 1 (g/L), ○ Concentration of component 2 (g/L), ○ Concentration of component 3 (g/L), and ○ Concentration of component 4 (g/L). • Plume_mass.out – plume mass output in both the low-k and transmissive zones. Data is output as: <ul style="list-style-type: none"> ○ Time (yrs), ○ Mass of component 1 in the low-k zone (kg), ○ Mass of component 1 in the transmissive zone (kg), ○ Mass of component 2 in the low-k zone (kg), ○ Mass of component 2 in the transmissive zone (kg), ○ Mass of component 3 in the low-k zone (kg), ○ Mass of component 3 in the transmissive zone (kg), ○ Mass of component 4 in the low-k zone (kg), ○ Mass of component 4 in the transmissive zone (kg). • REMChlor-MD.out – concentration in the transmissive zone. Data is output as: <ul style="list-style-type: none"> ○ Time (yrs), ○ X-direction location (m), ○ Y-direction location (m), |

REMCHLOR-MD RESULTS

| | |
|--|---|
| | <ul style="list-style-type: none">○ Z-direction location (m),○ Concentration for component 1 (g/L),○ Concentration for component 2 (g/L),○ Concentration for component 3 (g/L),○ Concentration for component 4 (g/L). |
|--|---|

CHEMICAL PARAMETER DATABASE

| Chemical Name | Organic Carbon Partitioning Coefficient (log (K _{oc}) @20-25 C) (log (1/kg))* | Solubility (@20-25 C) (mg/L)* |
|-----------------------------|---|-------------------------------------|
| Acetone | -0.24 | 1.00 × 10 ⁶ |
| Acenaphthene | 3.85 | 3.93 × 10 ⁰ |
| Acenaphthylene | 4.00 | 3.93 × 10 ⁰ |
| Anthracene | 4.15 | 4.50 × 10 ⁻² |
| Benzene | 1.58 | 1.75 × 10 ³ |
| Benzoic acid | 1.83 | 6.22 × 10 ⁴ |
| Benzo (a) Anthracene | 6.14 | 5.70 × 10 ⁻³ |
| Benzo (b) Fluoranthene | 5.74 | 1.47 × 10 ⁻² |
| Benzo (k) Fluoranthene | 5.74 | 4.30 × 10 ⁻³ |
| Benzo (g,h,i) Perylene | 6.20 | 7.00 × 10 ⁻⁴ |
| Benzo (a) Pyrene | 5.59 | 1.20 × 10 ⁻³ |
| Bromodichloromethane | 1.85 | 6.22 × 10 ¹ |
| Butanol, n- | 0.74 | 7.70 × 10 ⁴ |
| Carbon disulfide | 2.47 | 2.30 × 10 ³ |
| Carbon tetrachloride | 2.67 | 7.62 × 10 ² |
| Chlorobenzene | 2.46 | 4.45 × 10 ² |
| Chloroethane | 1.25 | 2.00 × 10 ⁴ |
| Chloroform | 1.93 | 9.64 × 10 ³ |
| Chloromethane | 1.40 | 4.00 × 10 ⁻³ |
| Chlorophenol, 2- | 2.11 | 2.85 × 10 ⁴ |
| Chrysene | 5.30 | 1.80 × 10 ⁻³ |
| Dibenzo (a,h) Anthracene | 5.87 | 5.00 × 10 ⁻⁴ |
| Dibromochloromethane | 2.05 | 5.25 × 10 ³ |
| Dichlorobenzene, (1,2) (-o) | 3.32 | 1.50 × 10 ² |
| Dichlorobenzene, (1,4) (-p) | 3.33 | 1.45 × 10 ² |
| Dichlorodifluoromethane | 2.12 | 1.98 × 10 ³ |
| Dichloroethane, 1,1- | 1.76 | 5.00 × 10 ³ |
| Dichloroethane, 1,2- | 1.76 | 8.69 × 10 ³ |
| Dichloroethene, cis1,2- | 1.38 | 8.00 × 10 ² |
| Dichloroethene, trans1,2- | 1.46 | 1.75 × 10 ³ |
| Ethylbenzene | 1.98 | 6.00 × 10 ² |
| Ethylene glycol | -0.90 | 1.00 × 10 ⁶ |
| Fluoranthene | 4.58 | 2.06 × 10 ⁻¹ |
| Fluorene | 3.86 | 1.69 × 10 ⁰ |
| Hexane, n- | 2.68 | 1.30 × 10 ¹ |
| Indeno (1,2,3,c,d) Pyrene | 7.53 | 7.17 × 10 ² |
| Methanol | -0.69 | 1.00 × 10 ⁶ |
| Methylene chloride | 1.23 | 1.54 × 10 ⁴ |
| Methyl ethyl ketone | 0.28 | 2.18 × 10 ⁵ |

CHEMICAL PARAMETER DATABASE

| Chemical Name | Organic Carbon Partitioning Coefficient (log (K _{oc}) @20-25 C) (log (1/kg))* | Solubility (@20-25 C) (mg/L)* |
|----------------------------|---|-------------------------------------|
| Methyl t-Butyl Ether | 1.08 | 4.80 × 10 ⁴ |
| Naphthalene | 3.11 | 3.29 × 10 ¹ |
| Phenanthrene | 4.15 | 1.60 × 10 ⁰ |
| Phenol | 1.44 | 9.30 × 10 ⁴ |
| Pyrene | 4.58 | 1.60 × 10 ⁻¹ |
| Tetrachloroethane 1,1,2,2- | 0.00 | 7.18 × 10 ² |
| Tetrachloroethene | 2.43 | 1.43 × 10 ² |
| Toluene | 2.13 | 5.15 × 10 ² |
| Trichlorobenzene | 3.91 | 3.03 × 10 ¹ |
| Trichloroethane 1,1,1- | 2.45 | 1.26 × 10 ³ |
| Trichloroethane 1,1,2- | 1.75 | 5.93 × 10 ³ |
| Trichloroethene | 1.26 | 1.00 × 10 ³ |
| Trichlorofluoromethane | 2.49 | 2.47 × 10 ³ |
| Vinyl Chloride | 0.39 | 2.54 × 10 ³ |
| Xylene (mixed isomers) | 2.38 | 1.98 × 10 ² |
| Xylene, m- | 3.20 | 1.58 × 10 ² |
| Xylene, o- | 2.11 | 1.75 × 10 ² |

* Values obtained from "Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface" by Wiedemeier *et al.*, 1999, Appendix B.

GEOLOGIC PARAMETER DATABASE

| Parameter | Value | Units |
|-------------------------------------|---|----------------------|
| Hydraulic Conductivity ¹ | | |
| Clean sands | 1×10^{-3} -1 | cm/s |
| Clays | $<1 \times 10^{-6}$ | cm/s |
| Gravels | >1 | cm/s |
| Silts | 1×10^{-6} - 1×10^{-3} | cm/s |
| Silty sands | 1×10^{-5} - 1×10^{-1} | cm/s |
| Total Porosity ² | | |
| Basalt | 0.03-0.35 | (-) |
| Clay | 0.34-0.60 | (-) |
| Coarse Gravel | 0.24-0.36 | (-) |
| Fine Gravel | 0.25-0.38 | (-) |
| Fine Sand | 0.26-0.53 | (-) |
| Coarse Sand | 0.31-0.46 | (-) |
| Limestone | 0.0-0.5 | (-) |
| Sandstone | 0.05-0.30 | (-) |
| Shale | 0.0-0.10 | (-) |
| Silt | 0.34-0.61 | (-) |
| Siltstone | 0.21-0.41 | (-) |
| Effective Porosity ³ | | |
| Clay | 0.01-0.20 | (-) |
| Fine Gravel | 0.2-0.35 | (-) |
| Medium Gravel | 0.15-0.25 | (-) |
| Coarse Gravel | 0.1-0.25 | (-) |
| Sandy Clay | 0.03-0.2 | (-) |
| Loess | 0.15-0.35 | (-) |
| Peat | 0.3-0.5 | (-) |
| Silt | 0.01-0.3 | (-) |
| Gravelly Sand | 0.2-0.35 | (-) |
| Fine Sand | 0.10-0.30 | (-) |
| Medium Sand | 0.15-0.30 | (-) |
| Coarse Sand | 0.20-0.35 | (-) |
| Glacial Sediments | 0.05-0.2 | (-) |
| Limestone | 0.01-0.24 | (-) |
| Unfractured Limestone | 0.001-0.05 | (-) |
| Sandstone | 0.1-0.4 | (-) |
| Siltstone | 0.01-0.35 | (-) |
| Fractured Granite | 0.00005-0.01 | (-) |
| Volcanic Tuff | 0.02-0.35 | (-) |
| Dry Bulk Density ² | | |
| Clay | 1.00-2.40 | (g/cm ³) |
| Silt | - | (g/cm ³) |

CHEMICAL PARAMETER DATABASE

| Parameter | Value | Units |
|-------------|-----------|----------------------|
| Granite | 2.24-2.46 | (g/cm ³) |
| Fine Sand | 1.37-1.81 | (g/cm ³) |
| Medium Sand | 1.37-1.81 | (g/cm ³) |
| Coarse Sand | 1.37-1.81 | (g/cm ³) |
| Sandstone | 1.60-2.68 | (g/cm ³) |
| Gravel | 1.36-2.19 | (g/cm ³) |
| Limestone | 1.74-2.79 | (g/cm ³) |

Notes:

1. From Newell *et al.*, 1996.
2. From Wiedemeier *et al.*, 1995.
3. From Wiedemeier *et al.*, 1999 (originally from Domenico and Schwartz, 1990 and Walton, 1998).

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TROUBLESHOOTING TIPS

Minimum System Requirements

REMChlor-MD model requires a computer system running Microsoft® Excel® (**2016 version 16.0.9226.2114 or newer**) for Windows. Operation requires an IBM-compatible PC equipped with a Pentium or later processor running at a minimum of 450 MHz. A minimum of 256 MB of system memory (RAM) is strongly recommended. Computers not meeting these recommendations will experience slow running times and/or problems with memory. REMChlor-MD versions are available for both the 32-bit and 64-bit versions of Excel (the default Excel installation is 32-bit).

Installation and Start-Up

The software is installed by unzipping the 32-bit or 64-bit Toolkit model file (REMChlorMD.zip) and keeping all the unzipped files in the same folder on your computer hard drive. To use the software, start Excel® and load the REMChlorMD.xlsb model file from the File / Open menu. You may see a message box that asks you whether you want to disable or enable the macros. For the Toolkit to operate effectively, you must *enable* the macros.

Spreadsheet-Related Problems

Backspace doesn't clear cell. Use the delete key on the keyboard or the mouse to clear data.

The buttons won't work. The Toolkit is built in the Excel® spreadsheet environment, and to enter data one must click anywhere outside the cell where data was just entered. If you can see the numbers you just entered in the data entry part of Excel® above the spreadsheet, the data have not yet been entered. Click on another cell to enter the data.

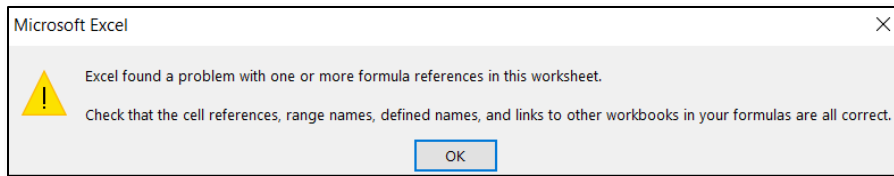
is displayed in a number box. The cell format is not compatible with the value (e.g., the number is too big to fit into the window). To fix this, select the cell, pull down the format menu, select *Format Cells* and click on the *Number* tab. Change the format of the cell until the value is visible. If the values still cannot be read, select the format menu, select *Cells*, and click on the *Font* tab. Reduce the font size until the value can be read.

#DIV/0! is displayed in a number box. The most common cause of this problem is that some input data are missing. In some cases, entering a zero in a box will cause this problem. Double check to make certain that data required for your run have been entered in all of the input cells.

#VALUE! is displayed in a number box. The most common cause of this problem is that some input data are missing. Double check to make certain that data required for your run have been entered in all of the input cells and all options have been selected.

Common Error Messages

Excel Found a Problem with One or More Formula References in this Worksheet: This error message often appears on the REMChlor-MD Output page. This is a harmless Excel error message that could not be coded out. Just click 'OK' to continue.



Unable to Load Help File: The most common error message encountered with the Toolkit is the message 'Unable to Open Help File' after clicking on a *Help* button. Depending on the version of Windows® you are using, you may get an Excel® Dialog Box, a Windows® Dialog Box, or you may see Windows® Help load and display the error. This problem is related to the ease with which the Windows® Help Engine can find the data file, REMChlorMD.chm. Here are some suggestions (in decreasing order of preference) for helping WinHelp find it:

- If you are asked to find the requested file, do so. The file is called REMChlorMD.chm, and it was installed in the same directory/folder as the REMChlor-MD model file (REMChlorMD.xlsm).
- Use the File/Open menus from within Excel® instead of double-clicking on the filename or Program Manager icon to open the REMChlor-MD model file. This sets the *current directory* to the directory containing the Excel® file you just opened.

ACKNOWLEDGEMENTS

This work was funded by the Environmental Security Technology Certification Program (ESTCP) project ER-201426.

The project team would like to thank all REMChlor-MD beta testers. Their invaluable input helped improve REMChlor-MD.

APPENDICES

APPENDIX 1. REMCHLOR-MD THEORETICAL BACKGROUND

REMChlor-MD Source Term

The following description of the source term in REMChlor-MD is extracted from the REMChlor User's Manual (Falta *et al.*, 2007). However, figure numbers have been formatted for this appendix.

Because direct measurement of source mass is not usually possible at field sites, quantitative data relating source mass to source discharge are limited. Two recent field source remediation experiments that used controlled DNAPL releases provide some insights into this relationship. Both of these experiments were conducted at the Dover National Test Facility at Dover Air Force Base. The first experiment, described by Brooks *et al.* (2002; 2004), used an ethanol flood to remediate a 51.2 kg controlled release of tetrachloroethylene (PCE). The experiment was performed in a 5m by 3m test cell that was created by driving sealable joint sheet pile walls through the ground into a confining clay layer located at a depth of about 12m. The DNAPL was released at different random locations in the cell, at a depth of about 10m, below the water table. Two injection wells, and six extraction wells were arranged in a double five-spot pattern to deliver the alcohol. The 40 day experiment resulted in the removal of about 64% of the PCE mass. Partitioning interwell tracer tests were used before and after the alcohol flood to measure the amount of DNAPL present in different swept zones. Dissolved PCE concentrations in these swept zones were also measured before and after the alcohol flood.

These field data points are plotted in Figure A1-1 as the blue squares, where the y-axis represents the groundwater concentration scaled to its pre-remediation value, and the x-axis is the PCE mass, scaled to its pre-remediation value. In a natural or pumped system, the discharge from the source zone would be proportional to this groundwater concentration. Although there is some variation in the response from the different swept zones, a general trend of decreasing dissolved concentration is seen as the PCE mass decreases. Several of these swept zone data suggest a 1:1 relationship between source mass reduction and source discharge reduction. Other swept zones showed a weaker response to the source mass reduction.

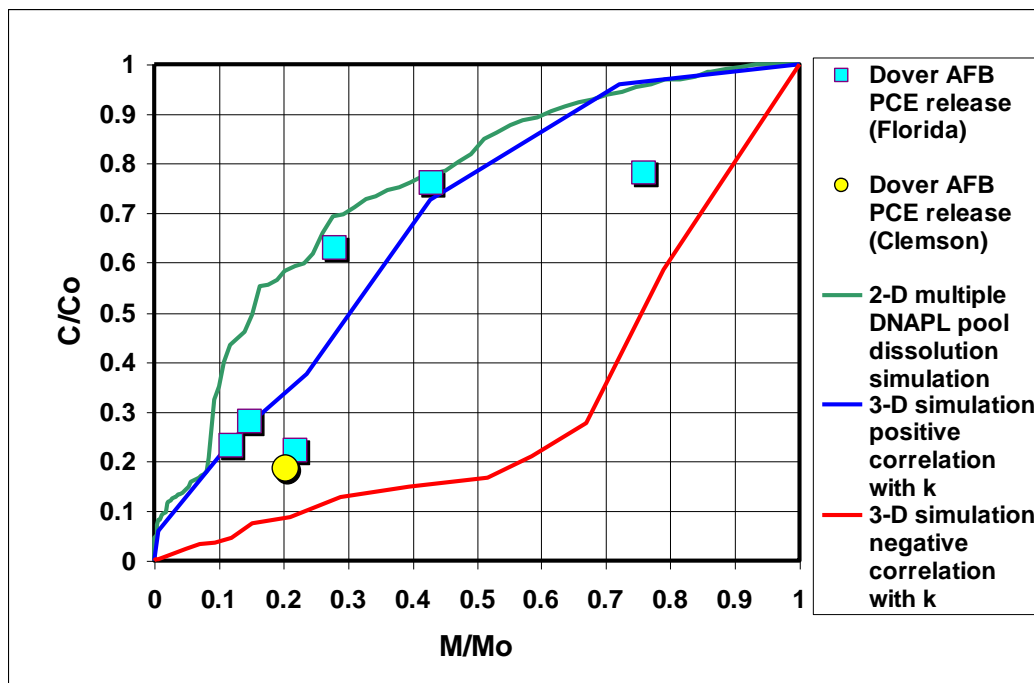


Figure A1-1. Source zone dissolved concentrations as a function of source zone DNAPL mass (from Falta *et al.*, 2005).

The second field experiment at the Dover site started with a controlled release of 92.3 kg of PCE, followed by a n-propanol alcohol flood (Falta *et al.*, 2003; Wood and Falta, 2003). They also used a double five spot flooding pattern and removed about 80% of the PCE mass from the test cell during the experiment. They conducted groundwater sampling from extraction wells before and after the remediation experiment using a line-drive groundwater flow pattern. These results indicated an approximately 80% reduction in the flowing groundwater concentration (Figure A1-1, yellow circle), suggesting a 1:1 relationship between source mass and source discharge.

A similar source mass/source discharge relationship has been observed in laboratory experiments. Fure *et al.* (2006) performed a series of four DNAPL dissolution experiments in two-dimensional flow cells with heterogeneous packing, using trichloroethylene (TCE) and 1,2-dichloroethane (DCA). These tests featured a segmented extraction well at one end of the tank to allow spatial resolution of the downstream source discharge (concentration). Each experiment consisted of the release of 10 ml of DNAPL into the upper part of the test cell, followed by water flushing until almost all of the DNAPL was removed. Although the individual extraction ports show somewhat variable responses over time, the integrated average of these produces a source mass/source discharge relationship that is fairly close to 1:1 (Fure *et al.*, 2006).

Multiphase flow numerical simulations have been used to explore the source mass/source discharge relationship. Falta (2003) showed a transient simulation of a hypothetical 2-D system composed of homogeneous media, and several distinct DNAPL pools. As water flows through this system, the DNAPL dissolves and is removed, leading to a gradual decline in concentration (discharge) at the outlet until most of the DNAPL is gone. This result is plotted in Figure A1-1 as the green line, and the curve is consistently above the 1:1 line. This means that a given reduction in source mass for this case produces a smaller reduction in source discharge.

Three-dimensional multiphase flow simulations using highly heterogeneous flow fields presented by Falta *et al.* (2005) suggest that the source mass/source discharge relationship depends largely on the correlation between the DNAPL distribution and the permeability. A simulation in which DNAPL was preferentially placed in high permeability materials produced a result where the scaled source discharge plotted above the 1:1 line with respect to scaled source mass (Figure A1-1, blue line). This means that a given fractional reduction in source mass would produce a smaller fractional reduction in the discharge. This behavior seems physically intuitive, because if most of the contaminant mass is located in a high permeability pathway, then most of it must be removed before the average discharge drops. An important feature of this type of source behavior is that it leads to relatively rapid depletion of the source by dissolution, with little tailing.

A simulation in which the DNAPL was correlated with low permeability produced the reverse result (Figure A1-1, red line); in this case the source discharge drops rapidly with mass removal, and the results plot below the 1:1 line. The physical interpretation of this case is that when most of the contaminant is trapped in low permeability, removing the small amount from the high permeability zones will have a big effect on the discharge. However, this type of source behavior also tends to lead to extensive tailing with time, because the source is never completely depleted by dissolution (Falta *et al.*, 2005). Transient simulations of DNAPL flow and dissolution in fractured clays produce a similar result (Falta, 2005). Following a release, the DNAPL is initially located in the fracture, but it can quickly dissolve and diffuse into the clay matrix (Parker *et al.*, 1994;1997; Ross and Lu, 1999; Slough *et al.*, 1999; Esposito and Thompson, 1999; O'Hara *et al.*, 200; Reynolds and Kueper, 2001; 2002; 2004; Parker *et al.*, 2004). Once a significant contaminant mass is found in the matrix, it may act as a very long term source to the fracture as it is flushed with clean water (Parker *et al.*, 1997; Esposito and Thompson, 1999; Reynolds and Kueper, 2002). When plotted in terms of a scaled discharge and a scaled mass, the numerical simulations produced curves that fell below the 1:1 line, indicating a rapid initial drop in discharge with source mass reduction, followed by extensive tailing.

The contaminant discharge from a source zone is the product of the flowrate of water passing through the source zone, and the average concentration of contaminant in that water (Figure A1-2). Source discharge thus has units of mass per time, and is not to be confused with mass flux, which is a discharge divided by an area. If water flows through the source at a rate of $Q(t)$, and if the mass in the source zone is also subject to some form of chemical or biological first order decay, then a mass balance on the source gives:

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

where M is the mass remaining in the source zone with time, $C_s(t)$ is the time-dependent source dissolved concentration (flow averaged), and λ_s is the source decay rate by processes other than dissolution. Water flow through the source may be due to infiltration (above the water table) or groundwater flow (below the water table).

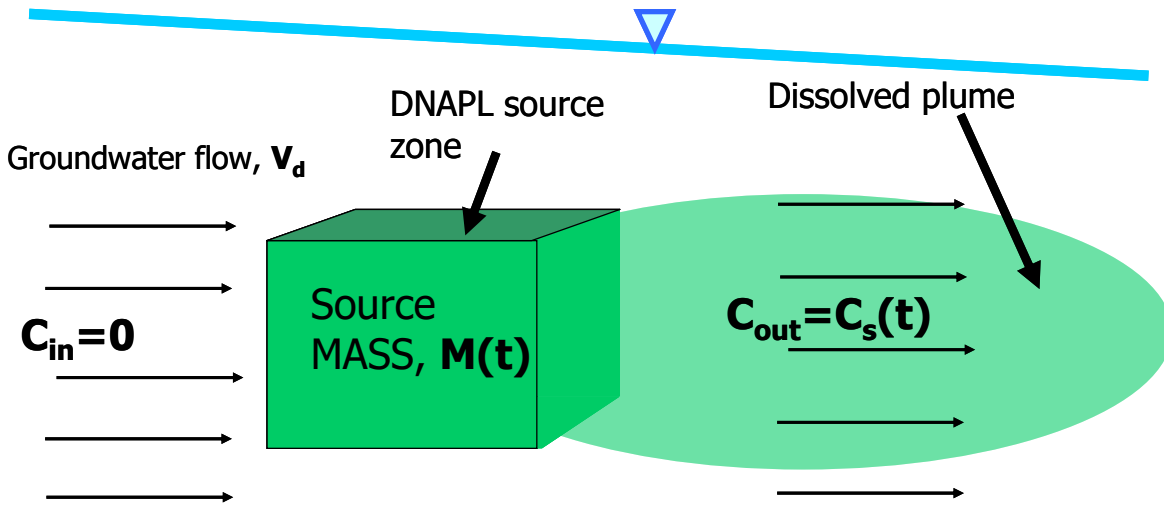


Figure A1-2. Conceptual model of source zone with time-dependent contaminant mass and discharge.

The source mass/source discharge relationships described earlier, and shown in Figure A1-1 can be roughly approximated by a simple power function (Rao *et al.*, 2001; Rao and Jawitz, 2003; Parker and Park, 2004; Zhu and Sykes, 2004; Falta *et al.*, 2005a):

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

The exponent, Γ , determines the shape of the source discharge response to changing source mass. If $\Gamma=1$, there is a 1:1 relationship (Figure A1-3). Values of Γ less than one produce C vs M curves that fall in the upper half of the graph (above the 1:1 line), while values of Γ greater than one produce C vs M curves that fall in the lower half of the graph. As shown previously, field and laboratory data suggest that a Γ value of one is reasonable in some cases, but theoretical analyses indicate that a range of Γ values are possible, depending mainly on the correlation of the contamination distribution to the permeability field.

Rao and Jawitz (2003) used a streamtube modeling approach to study the variation of source discharge with source mass. They assumed a heterogeneous collection of streamtube velocities that were log-normally distributed, with a uniform NAPL distribution. They found that as the standard deviation of the velocity field became

small, that the source discharge and source mass tended to be linearly related ($\Gamma \sim 1$). Parker and Park (2004) modeled a hypothetical DNAPL spill and dissolution in a three-dimensional, heterogeneous setting. They found that the best fit value of Γ was about 1.1 for the upper part of their simulation domain, and 0.4 in the lower part of the simulation domain. Figure A1-1 shows Equation (A2) plotted with $\Gamma = 0.5$ and 2 for comparison.

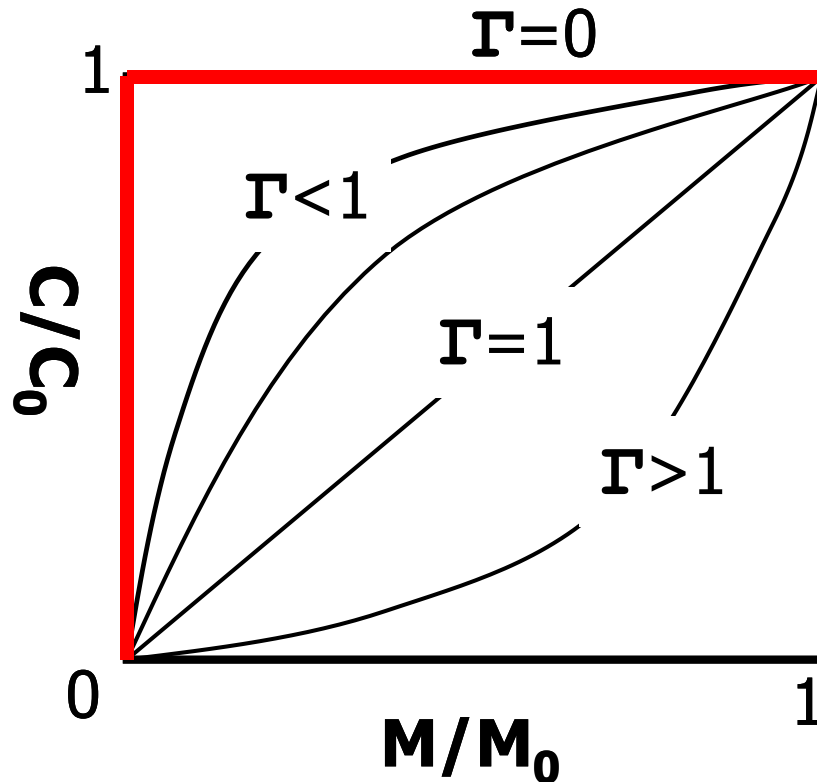


Figure A1-3. Power function representation of source mass/source discharge relationship (Equation 2).

If the water flow rate through the source zone in Equation (A1) is assumed to be constant, the power function (Equation 2) can be substituted to get:

$$\frac{dM}{dt} = -\frac{QC_0}{M_0^\Gamma} M^\Gamma - \lambda_s M \quad (3)$$

This equation is nonlinear for Γ values other than zero and one, but it can be linearized using Bernoulli's transformation, and solved to get (Falta *et al.*, 2005a):

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

Using Equation (2), this leads to the time-dependent source discharge function:

$$C_s(t) = \frac{C_0}{M_0^\Gamma} \left\{ \frac{-QC_0}{\lambda_s M_0^\Gamma} + \left(M_0^{1-\Gamma} + \frac{QC_0}{\lambda_s M_0^\Gamma} \right) e^{(\Gamma-1)\lambda_s t} \right\}^{\frac{\Gamma}{1-\Gamma}} \quad (5)$$

Similar expressions can be derived for the case of $\lambda_s=0$ (Parker and Park, 2004; Zhu and Sykes, 2004).

A very important special case of Equation (3) occurs when $\Gamma=1$ and $\lambda_s=0$. In that case, the differential equation is linear and may be integrated to get a simple exponential decay solution (Newell *et al.*, 1996; Parker and Park, 2004; Zhu and Sykes, 2004):

$$M(t) = M_0 e^{-\frac{QC_0 t}{M_0}} \quad (6)$$

and

$$C_s(t) = C_0 e^{-\frac{QC_0 t}{M_0}} \quad (7)$$

Therefore, when $\Gamma=1$, both the source mass and the source discharge will decline exponentially with time. If $\lambda_s=0$, then the apparent source decay rate due to dissolution is QC_0/M_0 , giving a source half-life of $.693M_0/(QC_0)$ (Newell and Adamson, 2005). This type of source behavior has been observed in the field at many chlorinated solvent sites (Newell and Adamson, 2005; McGuire *et al.*, 2006; Newell *et al.*, 2006), as well as at sites contaminated by petroleum hydrocarbons (Newell *et al.*, 2002). The widely used EPA BIOCHLOR (Aziz *et al.*, 2002) and BIOSCREEN (Newell *et al.*, 1996) analytic models for natural attenuation include exponentially decaying source terms.

An important characteristic of source zones with Γ greater than or equal to one, is that the source is never completely depleted, and the source discharge is always greater than zero, even at large times. In simple terms, this happens because the rate of discharge from the source drops as fast or faster than the rate of mass depletion of the source. When $\Gamma < 1$, the source has a finite life, and the source discharge eventually is equal to zero.

Another useful special case occurs when $\Gamma=0.5$. This leads to a source concentration that declines as a linear function of time (Falta *et al.*, 2005a; Newell and Adamson, 2005):

$$C_s(t) = C_0 - \frac{QC_0^2}{2M_0}t \quad (8)$$

and the source completely disappears at a time of

$$t = \frac{2M_0}{QC_0} \quad (9)$$

The simplest model of source behavior is one in which $\Gamma = 0$, which leads to a constant source discharge (concentration) until the source is fully depleted. This is also known as a “step function” model, and the source mass declines at a constant rate with respect to time.

The source model (Equations 4 and 5) represent source depletion by the natural process of dissolution and perhaps some other form of chemical or biological decay. This model can easily be modified to account for aggressive source remediation activities that remove a substantial fraction of the source mass over a short period of time (Falta *et al.*, 2005a). If a source remediation effort (such as alcohol or surfactant flooding, chemical oxidation, thermal treatment, air sparging) begins at a time of t_1 , and ends at a time of t_2 , during which a fraction, X of the source mass is removed, the functions can be simply rescaled. Then the source mass and concentration following remediation are given by:

$$M(t) = \left\{ \frac{-QC_2}{\lambda_s M_2^\Gamma} + \left(M_2^{1-\Gamma} + \frac{QC_2}{\lambda_s M_2^\Gamma} \right) e^{(\Gamma-1)\lambda_s(t-t_2)} \right\}^{\frac{1}{1-\Gamma}} \quad (10)$$

$$C_s(t) = C_2 \left(\frac{M(t)}{M_2} \right)^\Gamma \quad (11)$$

$$M_2 = (1-X)M_1 \quad (12)$$

$$C_2 = C_0 \left(\frac{(1-X)M_1}{M_0} \right)^\Gamma \quad (13)$$

where M_1 is the source mass at t_1 , and M_2 is the source mass at t_2 . The change in source discharge following remediation varies as the fraction of mass remaining $(1-X)$ raised to the power Γ . Therefore if $\Gamma = 1$, a linear reduction of source discharge is expected; if $\Gamma = 2$, the discharge will drop as the square of the mass fraction remaining, while if $\Gamma = 0.5$, the discharge will drop as the square root of the mass fraction remaining. Examples of this type of source behavior with and without remediation are shown in Figures A1-4 and A1-5, for a case where the initial source mass is 1620 kg, with an initial source concentration of 100 mg/l, and a water flow rate of 600 m³/yr.

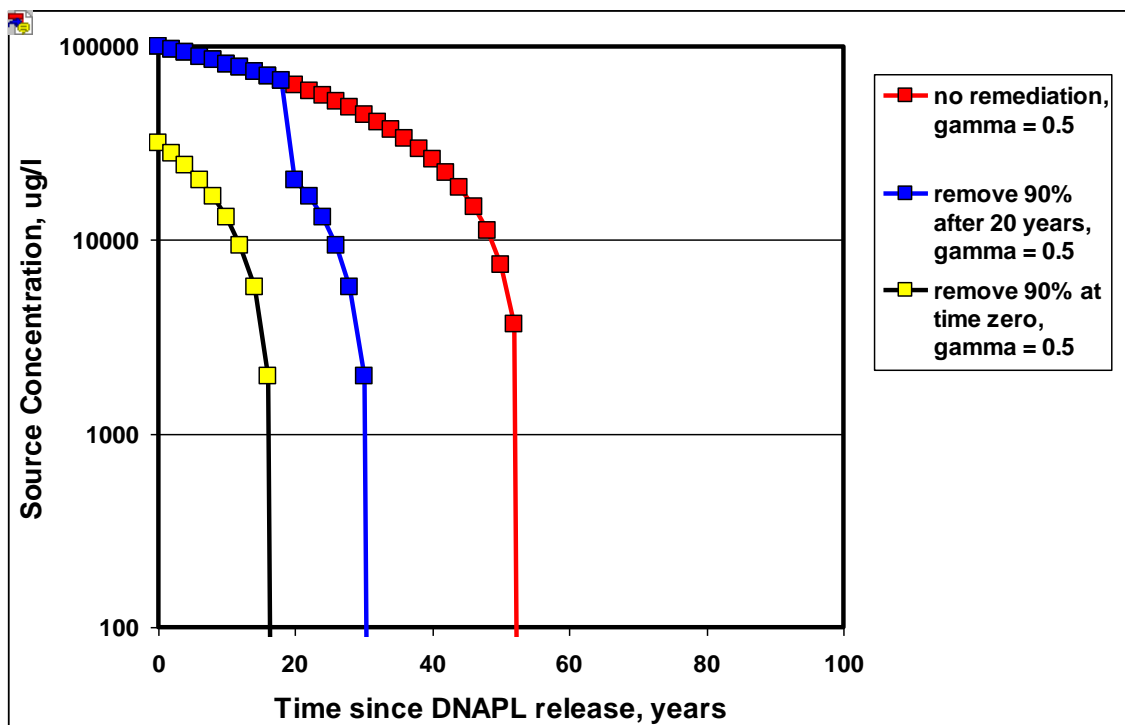


Figure A1-4. Source zone dissolved concentrations with and without source remediation for $\Gamma = 0.5$ (from Falta *et al.*, 2005a)

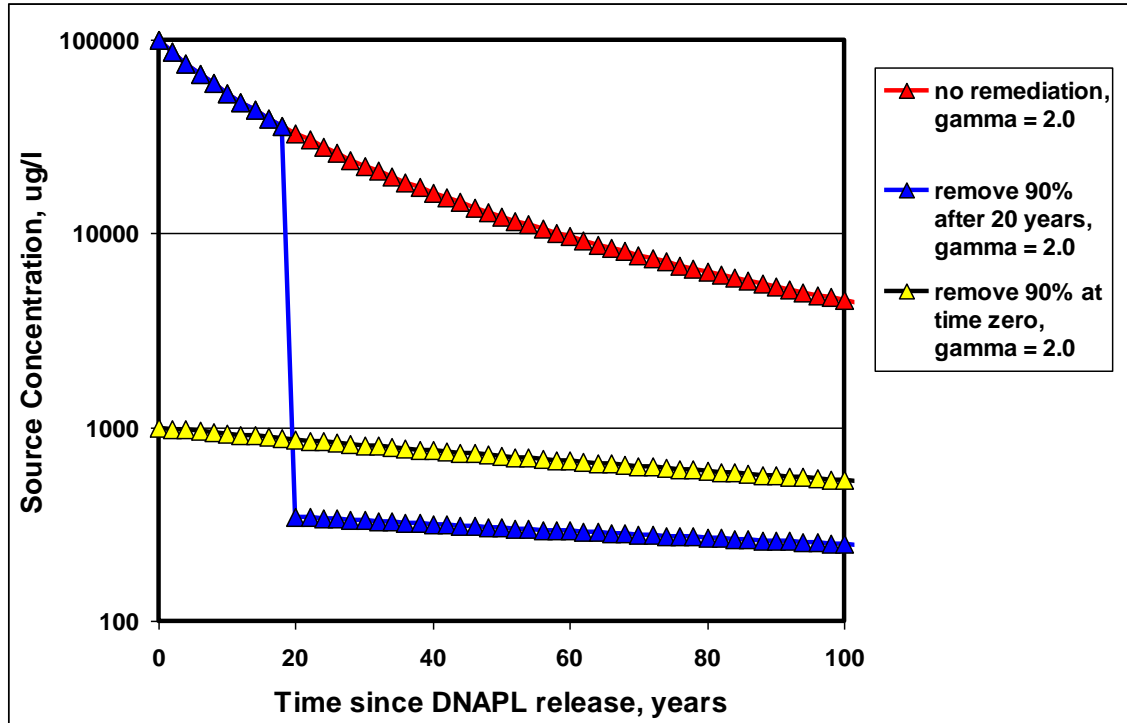


Figure A1-5. Source zone dissolved concentrations with and without source remediation for $\Gamma = 2.0$ (from Falta *et al.*, 2005a)

REMChlor-MD Plume Model with Matrix Diffusion (from Muskus and Falta, 2018)

Matrix diffusion in low permeability materials can be approximated as a one-dimensional process that depends on the distance from the interface with the high permeability material, z . The governing partial differential equations for transient matrix diffusion assuming first order decay of a component $m-1$ that produces a daughter compound, m are:

$$R_{lm} \frac{\partial C_{lm}}{\partial t} = \tau_l D \frac{\partial^2 C_{lm}}{\partial z_l^2} - \lambda_{lm} C_{lm} \quad \text{for } m = 1 \tag{14}$$

$$R_{lm} \frac{\partial C_{lm}}{\partial t} = \tau_l D \frac{\partial^2 C_{lm}}{\partial z_l^2} + y_{lm-1} \lambda_{lm-1} C_{lm-1} - \lambda_{lm} C_{lm} \quad \text{for } m > 1 \tag{15}$$

Here, the subscript l refers to the low permeability material. C_{lm} is the aqueous mass concentration of component m in the low permeability material, R_{lm} is the retardation factor of component m , τ_l is the tortuosity, D is the molecular diffusion coefficient, λ_{lm} is the first order decay rate of component m , and y_{m-1} is the mass yield of daughter component m from parent compound $m-1$. Equation (15) can be repeated for subsequent daughter products to form a complete decay chain. For example, at a site where tetrachloroethylene (PCE) undergoes decay to form trichloroethylene (TCE) and the TCE decays to form cis-1,2-dichloroethylene (DCE) which decays to form vinyl

chloride (VC), PCE would be the parent compound ($m=1$), governed by Equation (14), while TCE, DCE, and VC would be daughter compounds governed by Equation (15) with $m=2, 3$, and 4 , respectively.

The semi-analytical method is based on the thermal conduction approximation developed by Vinsome and Westerveld (1980). Bear *et al.* (1994) and Falta and Wang (2017) adapted the Vinsome and Westerveld model to the problem of matrix diffusion in a semi-infinite aquitard using the mathematical analogy between transient heat conduction and transient matrix diffusion. The approach is based on the use of a fitting function to describe the concentration profile as a function of distance from the interface in the low permeability matrix:

$$C_{lm}(z_l, t) = (C_m^{t+\Delta t} + p_m z_l + q_m z_l^2) e^{-z_l/d_m} \quad (16)$$

where $C_m^{t+\Delta t}$ is the current concentration of component m at the interface between high permeability and low permeability zones and p_m and q_m are fitting parameters. The concentration $C_m^{t+\Delta t}$ is the concentration that is solved for in each gridblock of a normal numerical simulation, and it is assumed to represent the average concentration in the high permeability part of the gridblock. The concentration penetration depth, d_m , is defined by:

$$d_m = \frac{\sqrt{\kappa_{lm} t}}{2}; \quad \kappa_{lm} = \frac{\tau_l D}{R_{lm}} \quad (17)$$

The zero level of the concentrations in Equation (16) correspond to the initial (uniform) concentrations in the low permeability zone, which is usually zero. The fitting parameters p_m and q_m are determined by two conservation of mass laws. The first constraint requires the fitting function to satisfy the governing equation at the high permeability/low permeability interface:

$$R_{lm} \left. \frac{\partial C_{lm}}{\partial t} = \tau_l D \frac{\partial^2 C_{lm}}{\partial z_l^2} \right|_{z_l=0} + y_{lm-1} \lambda_{lm-1} C_{lm-1} \Big|_{z_l=0} - \lambda_l C_{lm} \Big|_{z_l=0} \quad (18)$$

The component production term in Equation (5) is only used for daughter products ($m>1$).

In order to discretize the equation, a first-order finite difference approximation is applied to the time derivative. C_{lm} and C_{lm-1} are replaced with the trial functions on the right-hand side, which results in:

$$R_{lm} \left(\frac{C_m^{t+\Delta t} - C_m^t}{\Delta t} \right) = \tau_l D \left(\frac{C_m^{t+\Delta t}}{d_m^2} - \frac{2p_m}{d_m} + 2q_m \right) + y_{lm-1} \lambda_{lm-1} C_{m-1}^{t+\Delta t} - \lambda_{lm} C_m^{t+\Delta t} \quad (19)$$

The second constraint is the mass conservation of the components in the low permeability material. This requires that the rate of change of total mass in the matrix is to equal the mass flux across the interface minus the rate of decay in the matrix plus the rate of production in the matrix. For an ideal semi-infinite aquitard case, the integral of distance into low permeability areas is defined from zero to infinity (Falta and Wang, 2017). This study deals with finite embedded heterogeneities, such as low permeability lenses and layers or fractured porous media with parallel fractures. Thus, the mass conservation constraint must account for a finite diffusion distance. The characteristic average diffusion length, L corresponds to the average maximum depth or distance of

diffusion into the low permeability material. The low permeability matrix mass balance constraint becomes:

$$R_{lm} \frac{\partial}{\partial t} \int_0^L C_{lm} dz_l = -\tau_l D \left. \frac{\partial C_{lm}}{\partial z_l} \right|_{z_l=0} + y_{lm-1} \lambda_{lm-1} \int_0^L C_{lm-1} dz_l - \lambda_{lm} \int_0^L C_{lm} dz_l \quad (20)$$

The concentration integrals in Equation (20) are directly related to the mass of the components in the low permeability material. The solution of the concentration integrals in Equation (20) using the trial functions have the form:

$$I_m(t) = \int_0^L C_{lm} dz_l = C_m(t) d_m + p_m d_m^2 + 2q_m d_m^3 \quad (21)$$

$$-\left(C_m(t) d_m + p_m d_m L + p_m d_m^2 + q_m d_m L^2 + 2q_m d_m^2 L + 2q_m d_m^3 \right) e^{-L/d_m}$$

Following Pruess and Wu (1988, 1993), this integral can be written as a weighted function of $C_m(t)$, p_m , and q_m :

$$I_m(t) = \delta_m C_m(t) + \gamma_m p_m + \beta_m q_m \quad (22)$$

where

$$\delta_m = d_m - d_m e^{-L/d_m} \quad (23)$$

$$\gamma_m = d_m^2 - (d_m L + d_m^2) e^{-L/d_m} \quad (24)$$

$$\beta_m = 2d_m^3 - (L^2 d_m + 2d_m^2 L + 2d_m^3) e^{-L/d_m} \quad (25)$$

For the special case of an ideal infinite aquitard, where $L \rightarrow \infty$, $\delta_m = d_m$; $\gamma_m = d_m^2$; $\beta_m = 2d_m^3$, corresponding to the definition of $I(t)$ in Falta and Wang (2017). Replacing the derivative in Equation (20) with a finite difference approximation of the concentration integral, and substituting C_{lm} with the fitting functions in the space derivative and decay and production terms gives:

$$R_{lm} \left(\frac{\delta_m C_m^{t+\Delta t} + \gamma_m p_m + \beta_m q_m - I_m^t}{\Delta t} \right) = \tau_l D \left(\frac{C_m^{t+\Delta t}}{d_m} - p_m \right) + y_{lm-1} \lambda_{lm-1} I_{m-1}^{t+\Delta t} - \lambda_{lm} (\delta_m C_m^{t+\Delta t} + \gamma_m p_m + \beta_m q_m) \quad (26)$$

Solving the linear equations (19) and (26) by substitution provides the expressions for the fitting parameters p_m and q_m :

$$p_m = \frac{I_m^t + \frac{y_{lm-1} \lambda_{lm-1} I_{m-1}^{t+\Delta t} \Delta t}{R_{lm}} - EC_m^{t+\Delta t} - A_m \left(\frac{C_m^{t+\Delta t} - C_m^t}{2\kappa_{lm} \Delta t} - \frac{C_m^{t+\Delta t}}{2d_m^2} - \frac{y_{lm-1} \lambda_{lm-1} C_{m-1}^{t+\Delta t}}{2R_{lm} \kappa_{lm}} + \frac{\lambda_{lm} C_m^{t+\Delta t}}{2R_{lm} \kappa_{lm}} \right)}{\frac{A_m}{d_m} + B_m} \quad (27)$$

$$q_m = \frac{\frac{(C_m^{t+\Delta t} - C_m^t) d_m^2}{\kappa_{lm} \Delta t} - C_m^{t+\Delta t} + 2d_m p_m - \frac{y_{lm-1} \lambda_{lm-1} C_{m-1}^{t+\Delta t} d_m^2}{R_{lm} \kappa_{lm}} + \frac{\lambda_{lm} C_m^{t+\Delta t} d_m^2}{R_{lm} \kappa_{lm}}}{2d_m^2} \quad (28)$$

where

$$A_m = \beta_m + \frac{\lambda_{lm}\Delta t}{R_{lm}} \beta_m \quad (29)$$

$$B_m = \gamma_m + \kappa_{lm}\Delta t + \frac{\lambda_{lm}\Delta t}{R_{lm}} \gamma_m \quad (30)$$

$$E_m = \delta_m - \frac{\kappa_{lm}\Delta t}{d_m} + \frac{\lambda_{lm}\Delta t}{R_{lm}} \delta_m \quad (31)$$

Unique values of p_m and q_m are calculated in the aquifer gridblocks containing low permeability zones, and it is stored for use in the next time step (I_m^t). For the special case of diffusion in a semi-infinite aquitard with no reactions, the formulation becomes equivalent to the original Vinsome and Westerveld (1980) method for heat conduction and to the *Bear et al.* (1994) method for diffusion.

Calculation of Matrix Diffusion Mass Flow

The matrix diffusion mass flow entering (+) or leaving (-) the high permeability zone is described by Fick's first law of diffusion. Substituting the low permeability material concentration by the trial function:

$$\dot{m}_m = A_{md}\phi_l\tau_l D \left. \frac{\partial C_{lm}}{\partial z_l} \right|_{z_l=0} = A_{md}\phi_l\tau_l D \left(-\frac{C_m^{t+\Delta t}}{d_m} + p_m \right) \quad (32)$$

where ϕ_l is the porosity of the low permeability material and A_{md} is the matrix diffusion area, defined as the interfacial area between the high permeability and low permeability zones. The equation for p_m can be rewritten as:

$$p_m = a_m C_m^{t+\Delta t} + b_m \quad (33)$$

with

$$a_m = \frac{-E_m - \frac{A_m}{2\kappa_{lm}\Delta t} + \frac{A_m}{2d_m^2} - \frac{A_m\lambda_{lm}}{2R_{lm}\kappa_{lm}}}{\frac{A_m}{d_m} + B_m} \quad (34)$$

$$b_m^{t+\Delta t} = \frac{I_m^t + \frac{A_m C_m^t}{2\kappa_{lm}\Delta t} + \frac{A_m y_{lm-1} \lambda_{lm-1} C_{m-1}^{t+\Delta t}}{2R_{lm}\kappa_{lm}} + \frac{y_{lm-1} \lambda_{lm-1} I_{m-1}^{t+\Delta t} \Delta t}{R_{lm}}}{\frac{A_m}{d_m} + B_m} \quad (35)$$

Then the expression for the matrix diffusion mass flow rate, is:

$$\dot{m} = A_{md}\phi_l\tau_l D \left(\left(a_m - \frac{1}{d_m} \right) C_m^{t+\Delta t} + b_m^{t+\Delta t} \right) \quad (36)$$

The matrix diffusion mass flow becomes a linearly concentration dependent source/sink term added in the numerical transport model gridblocks that contain (or are adjacent to) low permeability materials. The $b_m^{t+\Delta t}$ term (Equation (35)) that appears in the gradient expression for component m does not depend on the current concentration of m , but it does depend on the previous concentration and integral of m , as well as on the current concentration and integral of the parent compound, $m-1$.

The semi-analytical approximation for matrix diffusion with a finite diffusion length does not force the concentration gradient at the symmetry boundary $z_l = L$ to be zero. This might seem to be a significant limitation of the formulation, but we have not found that to be true in practice, as evidenced by the comparisons in the following sections. It appears that it is sufficient to accurately represent the concentration gradient at the interface, and the mass balance in the low permeability material. This observation is similar to that made by Pruess and Wu (1993) in their study of heat conduction in cubic matrix blocks using a similar semi-analytic method. They tried adding a cubic term to the fitting function so that the additional free parameter could be used to force the concentration gradient to be zero at $z_l = L$, but found that this formulation gave less accurate results than the two parameter fitting function. They observed that forcing the zero gradient condition at $z_l = L$ resulted in a less accurate representation of the gradient at the interface.

Numerical Formulation

The diffusive mass flow given by Equation (36) can be added to implicit numerical transport models as a concentration dependent source/sink term. A key aspect of this method is that the numerical method only uses a mass balance on the high permeability part of the formation; the low permeability mass balance is maintained by the time-dependent concentration integrals for each component in each gridblock (Equation (9)).

There are two main geometrical configurations that are considered for the low permeability material. For the case of a semi-infinite aquitard that is adjacent to a high permeability aquifer, the aquifer is treated normally in the numerical formulation, and the matrix diffusion flux only occurs in the elements that are adjacent to the low permeability material (Falta and Wang, 2017). For the case of embedded low permeability heterogeneity, or in fractured systems, the volume fraction of the two materials in each gridblock must be specified. Denoting the volume fraction of the high permeability material as V_f , the volume of high permeability material in a gridblock of total volume V_i would be $V_f V_i$.

Using the integral finite difference method (Narasimhan and Witherspoon, 1976), the mass balance equation component m in the high permeability part of an element i is given by.

$$V_f V_i \frac{dM_{i,m}}{dt} = \sum_j F_{ij,m} A_{ij} + Q_{i,m} \quad (37)$$

where $M_{i,m}$ is the mass of component m per volume of high permeability material, $F_{ij,m}$ is the mass flux of m entering element i from neighboring elements j , A_{ij} is the interfacial area between elements i and elements j , and $Q_{i,m}$ is an internal source/sink term for m in element i . This source sink term accounts for decay and production reactions in the high permeability part of the gridblock, and for the matrix diffusion mass flow from the semi-analytical method (Equation (23)). The mass fluxes, F_m include advection and hydrodynamic dispersion (Freeze and Cherry, 1979; Fetter, 2008).

The mass term for each component in the high permeability material is:

$$M_m = \phi R_m C_m \quad (38)$$

Here, ϕ is the porosity of the high permeability material, and R_m is the solute retardation factor for component m in the high permeability material.

With the integral finite difference formulation, it is possible to use both structured and unstructured grids (see, for example, Panday et al, 2013). For the purpose of illustration, the transport equation using the semi-analytical approach was expressed for a three-dimensional system, using Cartesian coordinates. The system assumes uniform groundwater flow in the horizontal x -direction and dispersion in all three directions (i, j, k). First order parent-daughter decay/production is considered in the aqueous phase part of the high permeability material. A uniform grid with spacing of Δx , Δy , and Δz is assumed, along with a finite difference approximation for the concentration gradients in the dispersive fluxes, and upstream weighting for the advective term. Under these conditions, the discretized transport equation with a fully implicit formulation is:

$$\begin{aligned}
 & V_f \Delta x \Delta y \Delta z \phi R_m \left(\frac{C_{i,j,k,m}^{t+\Delta t} - C_{i,j,k,m}^t}{\Delta t} \right) = v_x \Delta y \Delta z (C_{i-1,j,k,m}^{t+\Delta t} - C_{i,j,k,m}^{t+\Delta t}) \\
 & + \frac{V_f \phi D_x \Delta y \Delta z}{\Delta x} (C_{i-1,j,k,m}^{t+\Delta t} - 2C_{i,j,k,m}^{t+\Delta t} + C_{i+1,j,k,m}^{t+\Delta t}) \\
 & + \frac{V_f \phi D_y \Delta x \Delta z}{\Delta y} (C_{i,j-1,k,m}^{t+\Delta t} - 2C_{i,j,k,m}^{t+\Delta t} + C_{i,j+1,k,m}^{t+\Delta t}) \\
 & + \frac{V_f \phi D_z \Delta x \Delta y}{\Delta z} (C_{i,j,k-1,m}^{t+\Delta t} - 2C_{i,j,k,m}^{t+\Delta t} + C_{i,j,k+1,m}^{t+\Delta t}) \\
 & + V_f \Delta x \Delta y \Delta z \phi y_{m-1} \lambda_{m-1} C_{i,j,k,m-1}^{t+\Delta t} - V_f \Delta x \Delta y \Delta z \phi \lambda_m C_{i,j,k,m}^{t+\Delta t} \\
 & + A_{md,i,j,k} \phi \tau_l D \left(\left(a_m - \frac{1}{d_m} \right) C_{i,j,k,m}^{t+\Delta t} + b_{i,j,k,m}^{t+\Delta t} \right)
 \end{aligned} \tag{39}$$

where v_x is the Darcy velocity in the horizontal direction, D_x , D_y , and D_z are dispersion coefficients in the x , y , and z directions, R_m is the component m retardation factor in the high permeability material, λ_m is the aqueous decay rate in the high permeability material, and y_{m-1} is the mass yield coefficient for production of m from decay of $m-1$ in the high permeability material. The Darcy velocity is defined on a total area basis, including both media, and the dispersive fluxes have been modified by including the high permeability volume fraction. The equations for the m components are coupled by the daughter production terms in both the high permeability and low permeability parts of the system.

The matrix diffusion area and volume fraction depend on the nature of the matrix diffusion geometry. If the gridblock does not contain any low permeability material, but it is adjacent to a semi-infinite aquitard, V_f is equal to 1, and $A_{md} = \Delta x \Delta y$. If the gridblock contains low permeability material, then $V_f < 1$, and A_{md} and L are determined by the geometry. The semi-analytical method has 3 geometrical parameters, but these can be reduced to two parameters by considering that the volume of low permeability material in a gridblock should be equal to the product of the matrix diffusion area and the characteristic average maximum diffusion length. Then

$$V_i(1 - V_f) = A_{md} L \tag{40}$$

and only two of the three parameters need to be specified.

APPENDIX 1. REMCHLOR-MD THEORETICAL BACKGROUND

Equation (39) gives a system of linear equations that can be solved by various methods. In the present work, a FORTRAN program was written using the Gauss Siedel iterative method. During each iteration, the computational method first updates the parent compound ($m=1$) in a gridblock, followed by the daughter products ($m=2,3,4\dots$) before moving to the next gridblock. With this ordering, the component production terms are calculated using the updated value of the parent concentration, $C_{m-1}^{t+\Delta t}$, in each gridblock.

Several examples of model verification, validation, and applications are shown in Falta and Wang (2017) and Muskus and Falta (2018).

APPENDIX 2. ESTIMATION OF MASS DISCHARGE IN T-ZONE

The mass discharge is calculated at each time-step as a function of distance down gradient from the source. This calculation neglects any dispersive flux, and only uses the advective mass flux. At every time-step, the calculation is performed for each x-location by taking the transmissive zone concentration and multiplying it by the darcy velocity and the gridblock area ($\Delta y \Delta z$) perpendicular to flow:

$$\bar{m}_{i,j,k,m}^{t+\Delta t} = v_x \Delta y \Delta z C_{i,j,k,m}^{t+\Delta t}$$

These are summed across the y-z plane to get the total discharge at that x location.

APPENDIX 3. CALCULATION OF MASS IN T-ZONE

The mass in the transmissive zone includes both the dissolved mass and the adsorbed mass. The mass in the transmissive part of each gridblock at each time-step is

$$mass_{i,j,k,m}^{t+\Delta t} = V_f \Delta x \Delta y \Delta z \phi R_m C_{i,j,k,m}^{t+\Delta t}$$

The mass in each gridblock is summed across the entire grid to get the total mass. This mass does not include any mass that is present in the source zone, which is located upstream of the numerical grid.

APPENDIX 4. CALCULATION OF MASS IN LOW-K ZONE

The mass in the low-K zone includes both the dissolved mass and the adsorbed mass. The low-K zone mass associated with gridblock may include mass that is present in embedded low-K zones inside the gridblock, as well as mass that has diffused into adjacent semi-infinite low K zones on the top or bottom (or both top and bottom) of the gridblock. For each gridblock, the low-K zone mass is calculated using the semi-analytic concentration integrals given by Equation 22 in Appendix 1. For a case where there are embedded low-K zones, the mass in each gridblock in the embedded low-K zone is:

$$mass(embedded)_{i,j,k,m}^{t+\Delta t} = A_{md} \phi_l R_{lm} I(embedded)_{i,j,k,m}^{t+\Delta t} \quad 1$$

If the element is adjacent to a low-K zone, and the semi-infinite approximation is used (top and bottom elements), the mass associated with the adjacent low-K zone is

$$mass(adjacent)_{i,j,k,m}^{t+\Delta t} = \Delta x \Delta y \phi_l R_{lm} I(adjacent)_{i,j,k,m}^{t+\Delta t} \quad 2$$

As a special case, if there is a single layer of gridblocks bounded above and below, then Equation 2 would be used twice. The total mass in the low-K zone is a sum of the masses calculated by Equations 1 and 2 over the entire grid. We have found that the semi-analytic method provides a very good mass balance in the low-K zone because the concentration integrals are stored at the end of each time-step for use in the next time-step, and a primary constraint of the method is enforcement of the mass balance in the low-K zone over a time-step.

APPENDIX 5. ESTIMATION OF CONCENTRATION IN OBSERVATION WELL

The concentration in an observation well is calculated by locating the gridblocks through which the well screen passes. The transmissive zone concentrations are averaged over these gridblocks to get the observation well concentration.

APPENDIX 6. ESTIMATION OF HETEROGENEITY PARAMETERS

The semi-analytical method requires 3 geometric parameters to simulate transient matrix diffusion in embedded low-K zones: transmissive zone volume fraction, average diffusion length, and surface area of low-k interfaces.

Unconsolidated Media

Transmissive Zone Fraction Volume

The transmissive zone fraction volume can be obtained from:

$$Volfrac = \frac{\sum_{i=1}^N (b_i - bl_i) / N}{\sum_{i=1}^N bl_i / N} \times 100 \quad (1)$$

where,

- $Volfrac$ = Transmissive zone volume fraction (%);
- b_i = Plume thickness (not counting any top or bottom low-k units) in the i^{th} boring log (L);
- bl_i = Total thickness of low-k units lying within the plume (not counting any low-k units at the top or bottom of the plume) in the i^{th} boring log (L); and
- N = Number of boring logs used for the estimation of the transmissive zone volume fraction

Average Diffusion Length

The average diffusion length can be obtained from a volume weighted average of individual low-K zone thicknesses. The average thickness is divided by 2 to account for symmetrical diffusion from the top and bottom of the low-K layers.

:

$$L = \frac{\sum_{i=1}^N 0.5 \times \left(\frac{\sum_{j=1}^n (bl_{ij})^2}{\sum_{j=1}^n bl_{ij}} \right)}{N} \quad (2)$$

where,

- L = Average diffusion length (L);
- bl_{ij} = Thickness of the j^{th} low-k unit lying within the plume (not counting any low-k units at the top or bottom of the plume) in the i^{th} boring log (L);
- N = Number of boring logs used for the estimation of the transmissive zone volume fraction; and
- n = Number of low-k units lying within the plume (not counting any low-k units at the top or bottom of the plume) in the i^{th} boring log.

Surface Area of Low-k Interfaces

APPENDIX 6. ESTIMATION OF HETEROGENEITY PARAMETERS

The surface area of low-k interfaces can be obtained from:

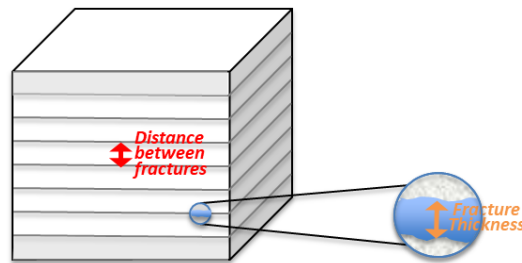
$$Amd = \frac{\Delta x \Delta y \Delta z (1 - \frac{Volfrac}{100})}{L} \quad (3)$$

where,

- Amd = Surface area of low-k interfaces (L^2);
- Δx = Model grid cell size in the x-direction (L);
- Δy = Model grid cell size in the y-direction (L);
- Δz = Model grid cell size in the z-direction (L);
- $Volfrac$ = Transmissive zone volume fraction calculated using Equation 1 (%); and
- L = Average diffusion length calculated using Equation 2 (L).

Fractured Rock/Media

The Toolkit uses a simplified conceptual model of a fractured rock/media system assuming parallel fractures.



Transmissive Zone Fraction Volume

The transmissive zone volume fraction can be obtained from:

$$Volfrac = b/a \times 100 \quad (4)$$

where,

- a = Typical distance between parallel fractures (L).
- b = Typical fracture aperture (L); and

Average Diffusion Length

The average diffusion length can be obtained from:

$$L = (a - b)/2 \quad (5)$$

Surface Area of Low-k Interfaces

The surface area of low-k interfaces can be obtained from:

APPENDIX 6. ESTIMATION OF HETEROGENEITY PARAMETERS

$$Amd = \frac{\Delta x \Delta y \Delta z (1 - \frac{Volfrac}{100})}{L} \quad (6)$$

where,

Volfrac = Transmissive zone volume fraction calculated using Equation 4 (%); and

L = Average diffusion length calculated using Equation 5 (L).



CASE STUDIES

CASE STUDY 1. INDUSTRIAL SITE, CONNECTICUT

Overview:

REMChlor-MD was used to estimate the effects of diffusion into and from low-k zones for the trichloroethene (TCE) plume at an industrial site in Connecticut (Figure 1.1) that was characterized and modeled to understand matrix diffusion in a classic paper by Chapman and Parker (2005).

For this purpose:

- Step 1: Initial values of all parameters, obtained from either Chapman and Parker (2005) or Parker *et al.* (2004), were entered into the Toolkit.
- Step 2: REMChlor-MD outputs were compared to 1) numerical model simulations, and 2) field-observed TCE concentrations. This step was critical in determining how well default Toolkit parameters predicted actual field conditions.
- Step 3: Input parameters were adjusted, as needed, to improve the comparisons.

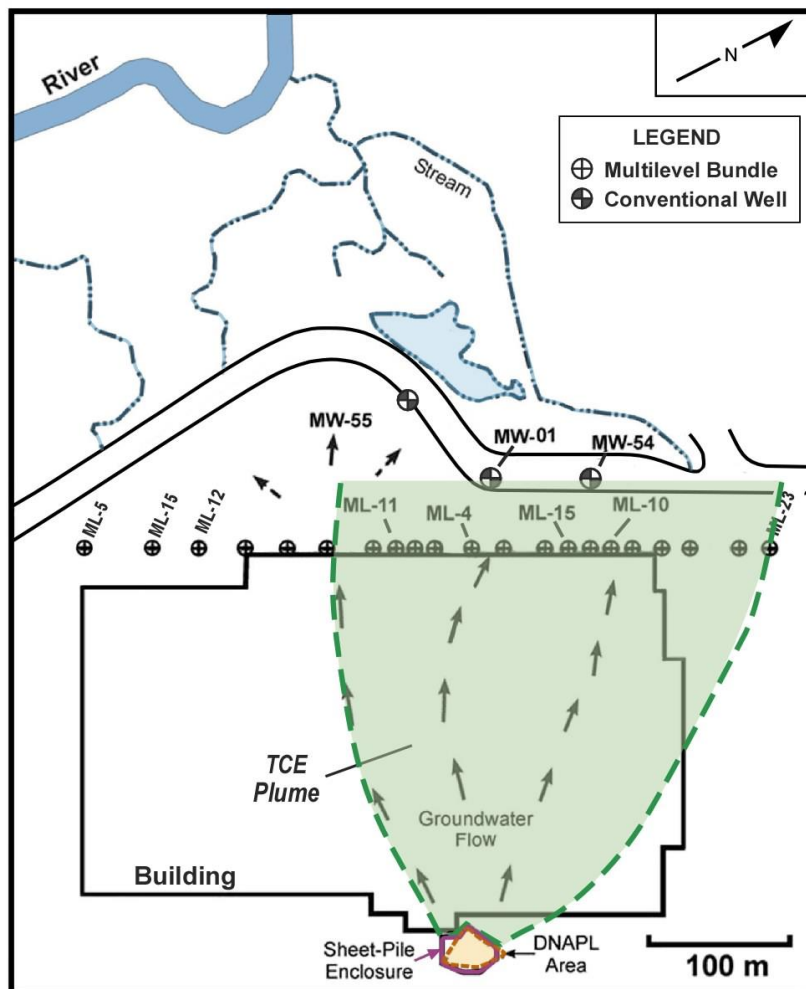


Figure 1.1. Site location map. Based on Chapman and Parker (2005) Figure 1.

Input Data:

| Data Type | Parameter | Value | Source of Data |
|------------------------------|--|--|--|
| Model Configuration | <ul style="list-style-type: none"> • X-direction model size: • Y-direction model size: • Z-direction model size: • Obs. well X-value: • Obs. well Y-value: • Obs. well Z-value top: • Obs. well Z-value bottom: • Starting year of simulation: • Ending year of simulation: | 330 (m) Numerical model comparison: 80 (m) Well comparison: 300 (m) Numerical model comparison: 1.5 (m) Well comparison: 1.5 (m) 330 (m) 0 (m) 1.5 (m) 0 (m) 1952 Numerical model comparison: 2092 Well comparison: 2011 | <ul style="list-style-type: none"> • Based on area of affected groundwater plume • Assumed for centerline comparison at the T-Zone/low-k zone interface • Based on area of affected groundwater plume • Based on Chapman and Parker, 2005 modeling, assumed same as well screen • Assumed same as well screen • Site History (e.g., Chapman and Parker, 2005) • Assumed along plume centerline • Site History • Site History • Site History • n/a |
| Media Characteristics | <ul style="list-style-type: none"> • Transmissive zone: • T-Zone K: • T-Zone porosity: • T-Zone tortuosity: • Low-k zone: • Low-k K: • Low-k porosity: • Low-k tortuosity: • T-Zone hydraulic gradient: | Sand 0.015 (cm/sec) 0.35 (-) 0.54 (-) Silt 1.41E-5 (cm/sec) 0.43 (-) 0.41 (-) 0.01 (-) | <ul style="list-style-type: none"> • Boring logs • Calculated based on site means • Site estimate • Literature (Toolkit default) • Boring logs • Literature (Toolkit default) • Site estimate • Literature (Toolkit default) • Site history |
| Heterogeneity | <ul style="list-style-type: none"> • Top/bottom plume conditions: • Heterogeneity parameters: | Matrix diffusion into an underlying low-k unit ; no top low-k unit. 0% embedded low-k material in T-zone | <ul style="list-style-type: none"> • Boring logs • Boring logs |
| Contaminants and Source Term | <ul style="list-style-type: none"> • Key constituents: • Initial source concentration: • Source mass: • T- Zone bulk density: • T-Zone fraction organic carbon: • Low-k zone bulk density: • Low-k. zone fraction organic carbon: • Organic carbon partitioning coefficient: | TCE Numerical model comparison: 1,100,000 (µg/L) Well comparison: 170,000 (µg/L) (calibrated) 75,000 (kg) 1.7 (g/mL) 0.038 (%) 1.5 (g/mL) 0.054 (%) 93.3 (L/kg) | <ul style="list-style-type: none"> • Site history • Literature TCE solubility • Estimated based on site history • Site estimate • Site estimate • Site evaluation • Site evaluation • Literature (Toolkit default) |

| Data Type | Parameter | Value | Source of Data |
|-------------------------|---|---|--|
| | <ul style="list-style-type: none"> • Source Width: • Source Z-value top: • Source Z-value bottom: • Molecular diffusion coefficient: | 39.3 (m) 0.2 (m) 0 (m) 9.1E-6 (cm ² /sec) | <ul style="list-style-type: none"> • Site map • Site information • Site information • Literature (Toolkit default) |
| Plume Degradation | <ul style="list-style-type: none"> • No plume degradation was modeled. | | |
| Plume Transport | <ul style="list-style-type: none"> • Longitudinal dispersivity: • Transverse dispersivity: • Vertical dispersivity: | 1 (m) 0.002 (m) 0.002 (m) | <ul style="list-style-type: none"> • Site information • Site information • Site information |
| Source Zone Remediation | <ul style="list-style-type: none"> • Percent mass removed: • Year remediation started: • Year remediation ended: • Gamma • Source decay: | 100 (%) 1994 1995 0 (-) 0 (1/yr) | <ul style="list-style-type: none"> • Site history • Site history • Assumed • Assumed source acting as step function • Assumed |
| Modeling Parameters | <ul style="list-style-type: none"> • Timestep size: • Number of iterations: • Convergence tolerance: • See Results every: | 1 (yr) 500 (-) 1.0E-2 (µg/L) 1 (yr) | <ul style="list-style-type: none"> • Assumed • Toolkit default • Toolkit default • n/a |

Summary:

- REMChlor-MD was used to estimate TCE groundwater concentrations in the transmissive zone following complete isolation of the DNAPL source zone at an industrial facility in 1994. The source zone start date was estimated to be 1952. Input parameters are shown on Figures 1.2a (comparison with numerical modeling) and 1.2b (comparison with field-observed TCE concentrations in MW-1).
- The surficial sandy aquifer at the site is underlain by a thick clayey silt aquitard. Heavy historical industrial pumping resulted in a long-term downward hydraulic gradient across the aquitard (Chapman and Parker, 2005) (note REMChlor-MD is unable to model vertical gradients through aquitards, so this process was not included in the REMChlor-MD modeling exercise).
- Two types of analysis were performed: 1) comparison of REMChlor-MD with the long-term, 140-year numerical modeling conducted by Chapman and Parker (2005), and 2) comparison of REMChlor-MD output with observed concentrations in a downgradient monitoring well for the period 1992 to 2005.
- Model configuration information was entered in Section 2, media characteristics in Section 3, heterogeneity data in Section 4, contaminants and source information in Section 5, plume degradation data in Section 6, plume transport parameters in Section 7, source zone remediation information in Section 8, and modeling parameters in Section 9.
- Site-specific values (as documented by Chapman and Parker, 2005) were available for all parameters except “molecular diffusion coefficient in free water”,

“tortuosity”, and “source” concentration. Toolkit default values were used for the molecular diffusion coefficient and tortuosity. The TCE solubility limit was used as the source concentration.

- Since exact source concentrations were unavailable, the TCE solubility limit was used as the starting point for source concentrations.
- A sheet pile enclosure was installed in 1994 around the DNAPL area (Figure 1.1).
- Monitoring data from well MW-01 was used for calibration.

KEY POINTS:

As shown in Figures 1.5 and 1.6, REMChlor-MD was able to reproduce the numerical model simulated and observed groundwater concentrations closely. REMChlor-MD compares well to Chapman and Parker’s more sophisticated modeling.

Since the exact history of the source concentration is unknown, the source concentration parameter was used as a calibration parameter for the comparison to observed concentrations in an actual monitoring well, MW-01 (Chapman and Parker, 2005). Specifically, initially, the source concentration was assumed to be the TCE solubility limit. During the calibration process, the concentration was adjusted to better match the observed concentrations at location MW-01 (Figure 1.6). Note that although only the source concentration was used as a calibration parameter for this evaluation, other combinations of input parameters could be adjusted to yield similar results. This shows that having actual data available for calibration improves the overall simulation results.

As shown in Figures 1.5 and 1.6, it is important to consider matrix diffusion when simulated plume lifetimes. The thin gray dashed lines (model results without matrix diffusion) show plume concentrations that are erroneously much lower than concentrations when matrix diffusion is considered (Figure 1.5) and when compared to the monitoring well data (Figure 1.6).

References

- Chapman S.W. and B.L. Parker, 2005. Plume persistence due to aquitard back diffusion following dense nonaqueous phase liquid source removal or isolation. *Water Resources Research* 41: W12411, doi: 10.1029/2005WR004224.
- Farhat, S.K., C.J. Newell, T.C. Sale, D.S. Dandy, J.J. Wahlberg, M.A. Seyedabbasi, J.M. McDade, and N.T. Mahler, 2012. Matrix Diffusion Toolkit, developed for the Environmental Security Technology Certification Program (ESTCP) by GSI Environmental Inc., Houston, Texas.

CASE STUDY 1: INDUSTRIAL SITE, CONNECTICUT

REMChlor-MD Data Input Screen Version 1.0 Beta

Site Location and ID: Connecticut Site (Chapman and Parker, 2005)

1. STARTING INFORMATION: SI Units, English Units, Unconsolidated, Fractured Rock/Media

2. MODEL CONFIGURATION

| | |
|---|------------|
| Cell Size | Model Size |
| X-Direction (in direction of groundwater flow): 2 | 330 (m) |
| Y-Direction (transverse to groundwater flow): 10 | 80 (m) |
| Z-Direction (vertical) (all layers have same hydrogeology): 0.1 | 1 (m) |

Observation Well Location: X-Value: 330.0 (m), Y-Value: 0.0 (m)
 Obs. Well Z-Value Top of Screen (model bottom is at Z=0): 1.5 (m), Bottom of Screen: 0.0 (m)
 Starting Year of Simulation: 1952 (YYYY year), Ending Year of Simulation: 2092 (YYYY year)

3. MEDIA CHARACTERISTICS (uniform for all cells)

| | | | |
|-----------|----------------------|--------------|----------------|
| Soil Type | Hydr. Cond. (cm/sec) | Porosity (-) | Tortuosity (-) |
| Sand | 1.50E-02 | 0.35 | 0.54 |
| Silt | 1.41E-05 | 0.43 | 0.41 |

T-Zone Hydraulic Gradient: 0.0100 (-)
 T-Zone Groundwater Darcy Velocity: 4.73E+01 (m/yr)

4. MATRIX DIFFUSION

| | |
|--|-----------------|
| Average Darcy Velocity (including low-k units) | 4.73E+01 (m/yr) |
| Transmissive Zone Volume Fraction | 1.00E+02 (%) |
| Average Diffusion Length | 0.00E+00 (m) |
| Surface Area of Low-k Interfaces | 0.00E+00 (m2) |

5. CONTAMINANTS AND SOURCE TERM

| | | | |
|--|--------------|--------------|--------------|
| Parent | Deg. Prod. 1 | Deg. Prod. 2 | Deg. Prod. 3 |
| Constituent (use dropdown menu): TCE | | | |
| Initial Source Concentration: 1.10E+06 | | | |
| Source Mass at Time of Release: 7.50E+04 | | | |
| Retardation Factor in T-Zone: 1.17 | | | |
| Retardation Factor in Low-k: 1.18 | | | |
| Source Width (REMChlor-MD will round to nearest whole cell): 39.3 (m) | | | |
| Z-Value for Top of Source (model bottom is at Z=0): 0.2 (m) | | | |
| Z-Value for Bottom of Source: 0 (m) | | | |
| General Molecular Diffusion Coefficient for all Constituents: 9.10E-06 | | | |

6. PLUME DEGRADATION (Both T-Zone and Low-k Zone)

| Time (yrs) | Distance From Source | | | |
|----------------------|----------------------------|----------------------------|----------------------------|-------------------------|
| | Zone 1 | Zone 2 | Zone 3 | Zone 4 |
| Period 3 (30.00 yrs) | Decay Rate (1,3): 0.00E+00 | Decay Rate (2,3): 0.00E+00 | Decay Rate (3,3): 0.00E+00 | T-Zone (1/yr): 0.00E+00 |
| Period 2 (2.00 yrs) | Decay Rate (1,2): 0.00E+00 | Decay Rate (2,2): 0.00E+00 | Decay Rate (3,2): 0.00E+00 | T-Zone (1/yr): 0.00E+00 |
| Period 1 (2.00 yrs) | Decay Rate (1,1): 0.00E+00 | Decay Rate (2,1): 0.00E+00 | Decay Rate (3,1): 0.00E+00 | T-Zone (1/yr): 0.00E+00 |

7. PLUME TRANSPORT

| | | |
|--------------|------------|----------|
| Longitudinal | Transverse | Vertical |
| 1 | 0.002 | 0.002 |

8. SOURCE ZONE REMEDIATION

| |
|---|
| Percent Source Mass Removed by Remediation: 100 (%) |
| Remediation Started in Year: 1994 (YYYY year) |
| Remediation Ended in Year: 1995 (YYYY year) |
| Mass-Flux/Remaining-Mass Term (Gamma, Γ): 0 (-) |
| Natural Source Decay Rate: 0 (1/yr) |

9. MODELING PARAMETERS

| |
|--|
| Timestep Size: 1 (yr) |
| Maximum Number of Iterations: 500 (-) |
| Convergence Tolerance: 1.00E-02 (ug/L) |
| See Results Every: 2 (yr) |

Buttons: Next Step: Show Graph, Show Previous Results, Return to Main Screen, New Site/Clear Data, Save/Export Data, Paste Example, Load Data, HELP

Figure 1.2a. REMChlor-MD input parameters for comparison with Chapman and Parker (2005) numerical model.

CASE STUDY 1: INDUSTRIAL SITE, CONNECTICUT

REMChlor-MD Data Input Screen Version 1.0 Beta

Site Location and ID: Connecticut Site (Chapman and Parker, 2005)

1. **STARTING INFORMATION** SI Units English Units Unconsolidated Fractured Rock/Media

2. **MODEL CONFIGURATION**

| Cell Size | Model Size |
|--|-------------|
| X-Direction (in direction of groundwater flow) | 2 330 (m) |
| Y-Direction (transverse to groundwater flow) | 10 300 (m) |
| Z-Direction (vertical) (all layers have same hydrogeology) | 0.1 1.5 (m) |

Observation Well Location: X-Value 330.0 (m) Y-Value 0.0 (m)
 Obs. Well Z-Value Top of Screen (model bottom is at Z=0) 1.5 (m) Bottom of Screen 0.0 (m)
 Starting Year of Simulation (year the source started) 1952 (YYYY year)
 Ending Year of Simulation (YYYY year) 2011

3. **MEDIA CHARACTERISTICS** (uniform for all cells)

| Soil Type | Hydr. Cond. (cm/seq) | Porosity (-) | Tortuosity (-) |
|------------------------------------|----------------------|--------------|----------------|
| Transmissive Zone (T-Zone) Sand | 1.50E-02 | 0.35 | 0.54 |
| Low Permeability Zone (Low-k) Silt | 1.41E-05 | 0.43 | 0.41 |

T-Zone Hydraulic Gradient 0.0100 (-)
 T-Zone Groundwater Darcy Velocity 4.73E+01 (m/yr)

4. **MATRIX DIFFUSION**

Average Darcy Velocity (including low-k units) 4.73E+01 (m/yr)
 Transmissive Zone Volume Fraction 1.00E-02 (%)
 Average Diffusion Length 0.00E+00 (m)
 Surface Area of Low-k Interfaces 0.00E+00 (m2)

5. **CONTAMINANTS AND SOURCE TERM**

| Parent | Deg. Prod. 1 | Deg. Prod. 2 | Deg. Prod. 3 |
|--|--------------------|--------------|--------------|
| Constituent (use dropdown menu) TCE | | | |
| Initial Source Concentration | 1.70E+05 | | |
| Source Mass at Time of Release | 7.50E+04 | | |
| Retardation Factor in T-Zone | 1.17 | | |
| Retardation Factor in Low-k | 1.18 | | |
| Source Width (REMChlor-MD will round to nearest whole cell) | 39.3 (m) | | |
| Z-Value for Top of Source (model bottom is at Z=0) | 0.2 (m) | | |
| Z-Value for Bottom of Source | 0 (m) | | |
| General Molecular Diffusion Coefficient for all Constituents | 9.10E-06 (cm2/seq) | | |

6. **PLUME DEGRADATION** (Both T-Zone and Low-k Zone)

| Time (yrs) | TCE Zone 1 | Component 2 Zone 2 | Component 3 Zone 3 | Component 4 |
|------------|------------------------------|------------------------------|------------------------------|-------------------------------|
| Period 3 | Decay Rate (1,3) 0.00E+00 | Decay Rate (2,3) 0.00E+00 | Decay Rate (3,3) 0.00E+00 | T-Zone (1/yr) Low-k (1/yr) |
| Period 2 | Decay Rate (1,2) 0.00E+00 | Decay Rate (2,2) 0.00E+00 | Decay Rate (3,2) 0.00E+00 | T-Zone (1/yr) Low-k (1/yr) |
| Period 1 | Decay Rate (1,1) 0.00E+00 | Decay Rate (2,1) 0.00E+00 | Decay Rate (3,1) 0.00E+00 | T-Zone (1/yr) Low-k (1/yr) |

7. **PLUME TRANSPORT**

Dispersivity (m) Longitudinal 1 Transverse 0.002 Vertical 0.002

8. **SOURCE ZONE REMEDIATION**

Percent Source Mass Removed by Remediation 100 (%)
 Remediation Started in Year 1994 (YYYY year)
 Remediation Ended in Year 1995 (YYYY year)
 Mass-Flux/Remaining-Mass Term (Gamma, Γ) 0 (-)
 Natural Source Decay Rate 0 (1/yr)

9. **MODELING PARAMETERS**

| | |
|------------------------------|-----------------|
| Timesstep Size | 1 (yr) |
| Maximum Number of Iterations | 500 (-) |
| Convergence Tolerance | 1.00E-02 (ug/L) |
| See Results Every | 2 (yr) |

Next Step: Show Graph | Show Previous Results | New Site/Clear Data | Paste Example | Return to Main Screen | Save/Export Data | Load Data | HELP

Figure 1.2b. REMChlor-MD input parameters for comparison with observed concentrations in monitoring well MW-01.

REMChlor-MD Heterogeneity Calculator - Fractured Rock/Media Version 1.0 Beta

STEP 1. Pick One of These Three Basic Top/Bottom Conditions for Your Plume

No Matrix Diffusion in Under- and Overlying Low-k Units

Matrix Diffusion in Underlying Low-k

Matrix Diffusion in Overlying Low-k

Matrix Diffusion in Under- and Overlying Low-k Units

Hydrogeology Type

Location of Matrix Diffusion

Hydrogeology Type

Location of Matrix Diffusion

Next:
Go to Step 2

Return to Main
Input Screen

HELP

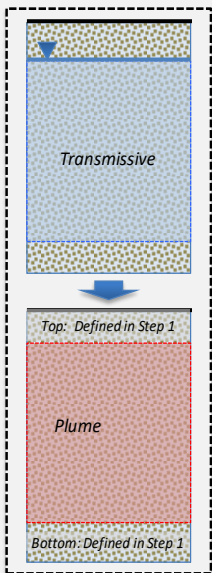
Figure 1.3. REMChlor-MD heterogeneity input parameters – location of matrix diffusion.

REMChlor-MD Heterogeneity Calculator - Unconsolidated Media
Version 1.0 Beta

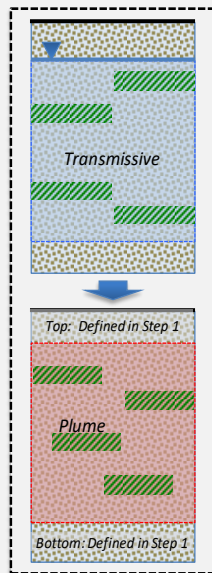
STEP 2. Pick an option for the embedded layering between the top and bottom of your plume that best represents your Site.
(Note: Don't count the top and bottom Low-k layers; just the in-between embedded layers.)

Simple Method: Pick one of these five options:

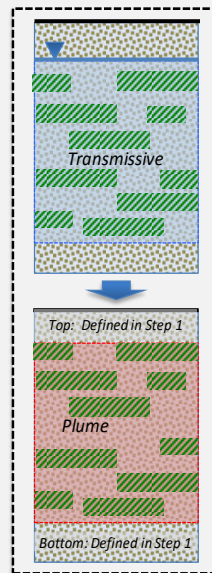
~0% of Plume Thickness is in Low-k Material (not counting top, bottom layers)



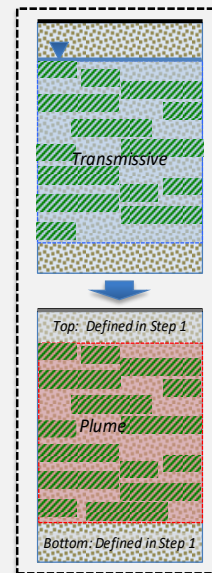
~20% of Plume Thickness is in Low-k Material (not counting top, bottom layers)



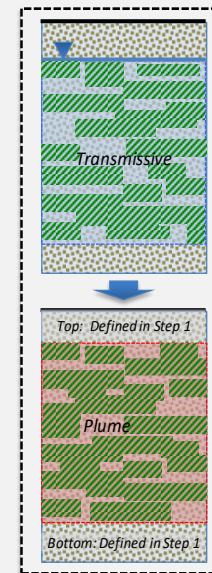
~40% of Plume Thickness is in Low-k Material (not counting top, bottom layers)



~60% of Plume Thickness is in Low-k Material (not counting top, bottom layers)



~80% of Plume Thickness is in Low-k Material (not counting top, bottom layers)



OR pick one of these two options:

- Use Site-Specific Data (More complicated, but more accurate)
- Enter Heterogeneity Parameters Manually

**Next:
Go to Step 3**

Return to Step 1

Return to Main Input Screen

HELP

Figure 1.4. REMChlor-MD heterogeneity input parameters – embedded low-k material layering.

REMCHLOR-MD TOOLKIT
 ▼ USER'S MANUAL ▼

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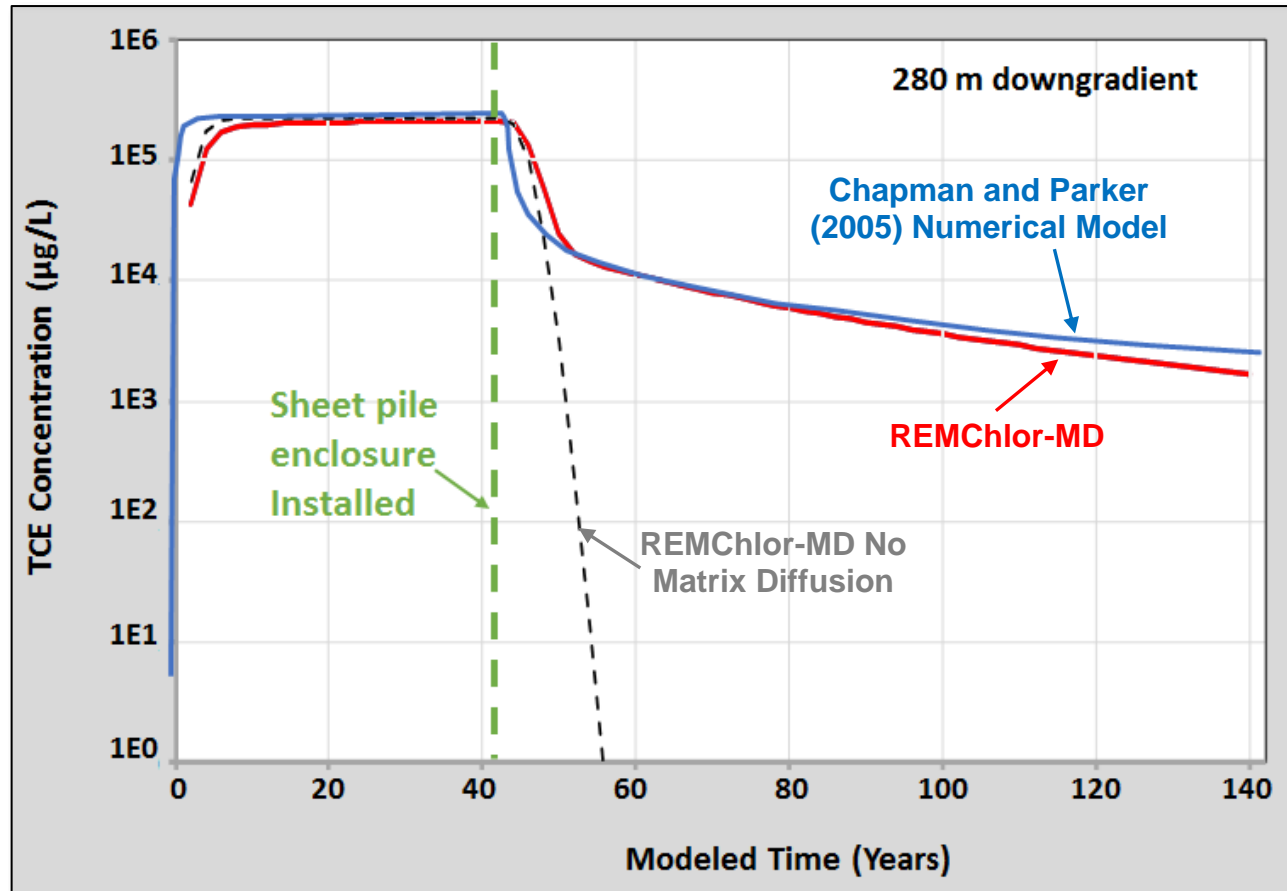


Figure 1.5. Comparison of REMChlor-MD (red line) and Chapman and Parker (2005) numerical model simulation (blue line) outputs showing a close match between the two modeling simulations over a 140 year time span. The dashed gray line is a REMChlor-MD simulation where the matrix diffusion process in the plume has been turned off. The gray line shows that without inclusion of the matrix diffusion process, the predicted plume cleanup time is too low (i.e., too optimistic).

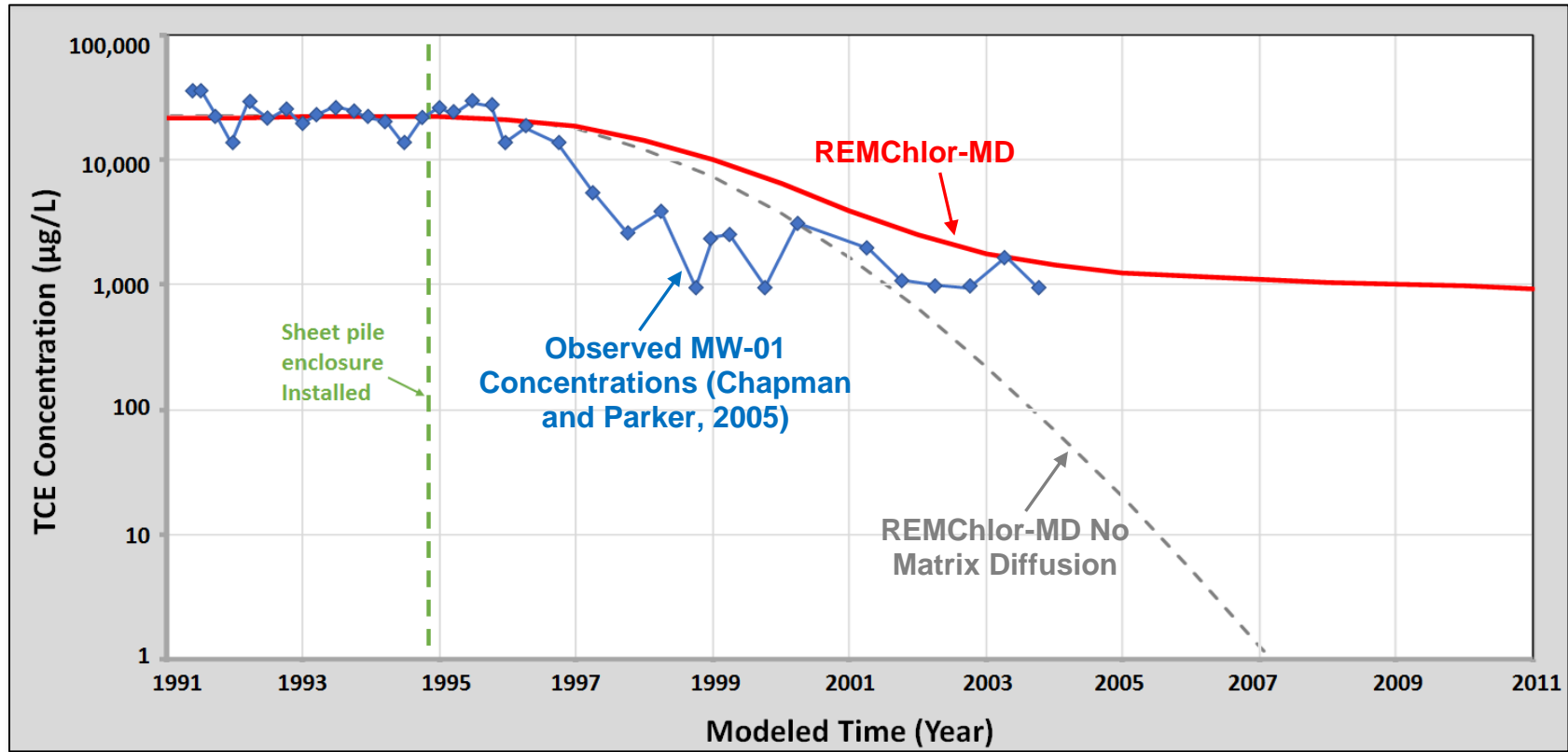


Figure 1.6. Comparison of REMChlor-MD output (red line) and data from a monitoring well (Chapman and Parker, 2005; blue line with diamond symbols). A REMChlor-MD simulation *without* matrix diffusion (dashed gray line) does not match the data from the monitoring well and shows the importance of considering matrix diffusion in the plume for this site.

CASE STUDY 2. FORMER INDUSTRIAL SITE, NE USA

Overview:

REMChlor-MD was used to estimate the effects of matrix diffusion through a fractured bedrock system for the trichloroethene (TCE) plume at a former industrial site in northeastern United States analyzed and modeled by Lipson *et al.* (2005).

For this analysis:

- Step 1: Initial values of all parameters, obtained from Lipson *et al.* (2005), were entered into the Toolkit.
- Step 2. REMChlor-MD outputs were compared to TCE concentrations simulated by Lipson *et al.* (2005). This step was critical in determining how well default Toolkit parameters predicted actual field conditions.

Input Data:

| Data Type | Parameter | Value | Source of Data |
|------------------------------|--|---|--|
| Model Configuration | <ul style="list-style-type: none"> • X-direction model size: • Y-direction model size: • Z-direction model size: • Obs. well X-value: • Obs. well Y-value: • Obs. well Z-value top: • Obs. well Z-value bottom: • Starting year of simulation: • Ending year of simulation: | <ul style="list-style-type: none"> 300 (m) 100 (m) 25 (m) 300 (m) 50 (m) 3 (m) 0 (m) 1955 2025 | <ul style="list-style-type: none"> • Site information (e.g., Lipson <i>et al.</i>, 2005) • Site information • Site information • Assumed • Assumed along plume centerline • Assumed 10-ft screen • Assumed 10-ft screen • Assumed based on site information • n/a |
| Media Characteristics | <ul style="list-style-type: none"> • Hydrogeologic setting: • Bulk K: • Fracture porosity: • Fracture tortuosity: • Matrix porosity: • Fracture tortuosity: • Hydraulic gradient: | <ul style="list-style-type: none"> Fractured Sandstone 1.58E-4 (cm/sec) 1 (-) 1 (-) 0.077 (-) 0.2 (-) 0.005 (-) | <ul style="list-style-type: none"> • Site information • Site information • Literature (Toolkit default) • Literature (Toolkit default) • Site information • Site information • Site information |
| Heterogeneity | <ul style="list-style-type: none"> • Top/bottom plume conditions: • Distance between fractures: • Aperture/fracture thickness: | <ul style="list-style-type: none"> No matrix diffusion in any under- and overlying low-k units 1.42 (m) 1.40E-4 (m) | <ul style="list-style-type: none"> • Site information • Site information • Site information |
| Contaminants and Source Term | <ul style="list-style-type: none"> • Key constituent: • Initial source concentration: • Source mass: • Fracture retardation factor: • Matrix retardation factor: • Source Width: • Source Z-value top: | <ul style="list-style-type: none"> TCE 780,000 (µg/L) 1000 (kg) 1 15.7 50 (m) 25 (m) | <ul style="list-style-type: none"> • Site information • Site information • Assumed • Site information • Site information • Assumed • Assumed |

| Data Type | Parameter | Value | Source of Data |
|-------------------------|---|--|--|
| | <ul style="list-style-type: none"> • Source Z-value bot: • Molecular diffusion coefficient: | 0 (m) 1.0E-9 (m ² /sec) | <ul style="list-style-type: none"> • Assumed • Site information |
| Plume Degradation | <ul style="list-style-type: none"> • No plume degradation was modeled. | | |
| Plume Transport | <ul style="list-style-type: none"> • Longitudinal dispersivity: • Transverse dispersivity: • Vertical dispersivity: | 0.3 (m) 0.03 (m) 0.003 (m) | <ul style="list-style-type: none"> • Site information • Assumed 1/10 of longitudinal dispersivity • Assumed 1/100 of longitudinal dispersivity |
| Source Zone Remediation | <ul style="list-style-type: none"> • Percent mass removed: • Year remediation started: • Year remediation ended: • Gamma • Source decay: | 100 (%) 1992 1993 0 (-) 0 (1/yr) | <ul style="list-style-type: none"> • Site information • Site information • Assumed • Assumed source acting as step function • Assumed |
| Modeling Parameters | <ul style="list-style-type: none"> • Timestep size: • Number of iterations: • Convergence tolerance: • See Results every: | 0.1 (yr) 500 (-) 1.0E-2 (µg/L) 1 (yr) | <ul style="list-style-type: none"> • Toolkit default • Toolkit default • Toolkit default • n/a |

Summary:

- REMChlor was used to estimate TCE concentrations due to matrix diffusion after hypothetical complete removal of the source in a fractured rock system modeled by Lipson *et al.* 2005). Input parameters are shown on Figure 2.1 through 2.3 and comparisons of the Toolkit simulated and Lipson *et al.* reported concentrations on Figures 2.4 and 2.5.
- Model configuration information was entered in Section 2, media characteristics in Section 3, heterogeneity data in Section 4, contaminants and source information in Section 5, plume degradation data in Section 6, plume transport parameters in Section 7, source zone remediation information in Section 8, and modeling parameters in Section 9.
- Site-specific values (as documented by Lipson *et al.* (2005)) were used for the majority of parameters.
- The REMChlor-MD model was not calibrated.

KEY POINTS:

The purpose of this evaluation was to determine how well REMChlor-MD could simulate solute transport in a fractured rock system consisting of equally spaced parallel fractures.

REMChlor-MD was able to reproduce Lipson *et al.*'s simulated concentrations very well at both before the start of source remediation and twenty years after source remediation (Figures 2.4 and 2.5). Therefore, no adjustment of any input parameters was necessary.

REMChlor-MD modeled concentrations were within an order of magnitude at the maximum modeled distance of 300 m.

REMChlor-MD runs *without* matrix diffusion (the thin dashed gray lines in Figures 2.4 and 2.5) erroneously show dramatically higher plume concentrations before remediation (because matrix diffusion removes contaminants from the fractures) and much lower plume concentrations 20 years after remediation (because there is no back diffusion adding contaminant to the fractures). For this fractured rock site with fractures in a sedimentary matrix, matrix diffusion is a key process in understanding the impact of source remediation on downgradient plume concentrations and on how quickly the plume will clean up after source remediation.

References

Lipson, D.S., B.H. Kueper, and M.J. Gefell, 2005. Matrix Diffusion-Derived Plume Attenuation in Fractured Rock, *Ground Water* 43(1): 30-39.

CASE STUDY 2: FORMER INDUSTRIAL SITE, NE USA

REMChlor-MD Data Input Screen

Version 1.0 Beta

Site Location and ID: **NE USA Fractured Rock Site (Lipsom et al. 2005)**

1. STARTING INFORMATION SI Units English Units Unconsolidated Fractured Rock/Media

2. MODEL CONFIGURATION

Cell Size: X=5, Y=5, Z=5 (m)

Model Size: X=300, Y=100, Z=25 (m)

Observation Well Location: X=300.0, Y=50.0, Z=3.0 (m)

Starting Year of Simulation: 1955 (YYYY year)

Ending Year of Simulation: 2025 (YYYY year)

3. MEDIA CHARACTERISTICS (uniform for all cells)

Soil Type: Sandstone, Bulk K: 1.58E-04 (cm/sec)

Fracture Porosity: 1, Tortuosity: 1.00

Hydraulic Gradient: 0.0050 (-), Bulk Groundwater Darcy Velocity: 2.49E-01 (m/yr)

4. MATRIX DIFFUSION

Bulk Groundwater Darcy Velocity: 2.49E-01 (m/yr)

Fracture Volume Fraction: 9.86E-03 (%)

Average Diffusion Length: 7.10E-01 (m)

Surface Area of Matrix Interfaces: 1.76E+02 (m2)

5. CONTAMINANTS AND SOURCE TERM

Constituent: TCE

Initial Source Concentration: 7.80E+05 (ug/L)

Source Mass at Time of Release: 1.00E+04 (kg)

Retardation Factor in T-Zone: 1

Retardation Factor in Low-k: 15.7

Source Width: 50 (m)

Z-Value for Top of Source: 25 (m)

Z-Value for Bottom of Source: 0 (m)

General Molecular Diffusion Coefficient for all Constituents: 1.00E-09 (m2/sec)

6. PLUME DEGRADATION (Both T-Zone and Low-k Zone)

Distance from Source

| Time (YYYY year) | TCE Zone 1 | Component 2 Zone 2 | Component 3 Zone 3 | Component 4 |
|------------------|------------------------------|------------------------------|------------------------------|-------------------------------|
| Period 3 (2024) | Decay Rate (1,3) 0.00E+00 | Decay Rate (2,3) 0.00E+00 | Decay Rate (3,3) 0.00E+00 | T-Zone (1/yr) Low-k (1/yr) |
| Period 2 (1956) | Decay Rate (1,2) 0.00E+00 | Decay Rate (2,2) 0.00E+00 | Decay Rate (3,2) 0.00E+00 | T-Zone (1/yr) Low-k (1/yr) |
| Period 1 | Decay Rate (1,1) 0.00E+00 | Decay Rate (2,1) 0.00E+00 | Decay Rate (3,1) 0.00E+00 | T-Zone (1/yr) Low-k (1/yr) |

7. PLUME TRANSPORT

Dispersivity (m): Longitudinal: 0.3, Transverse: 0.03, Vertical: 0.003

8. SOURCE ZONE REMEDIATION

Percent Source Mass Removed by Remediation: 100 (%)

Remediation Started in Year: 1992 (YYYY year)

Remediation Ended in Year: 1993 (YYYY year)

Mass-Flux/Remaining-Mass Term (Gamma, Γ): 0 (-)

Natural Source Decay Rate: 0 (1/yr)

9. MODELING PARAMETERS

Timestep Size: 0.1 (yr)

Maximum Number of Iterations: 500 (-)

Convergence Tolerance: 1.00E-02 (ug/L)

See Results Every: 1 (yr)

Buttons: Next Step: Show Graph, Show Previous Results, New Site/Clear Data, Paste Example, HELP, Return to Main Screen, Save/Export Data, Load Data

Figure 2.1. REMChlor-MD input parameters.

REMChlor-MD Heterogeneity Calculator - Fractured Rock/Media

Version 1.0 Beta

STEP 1. Pick One of These Three Basic Top/Bottom Conditions for Your Plume

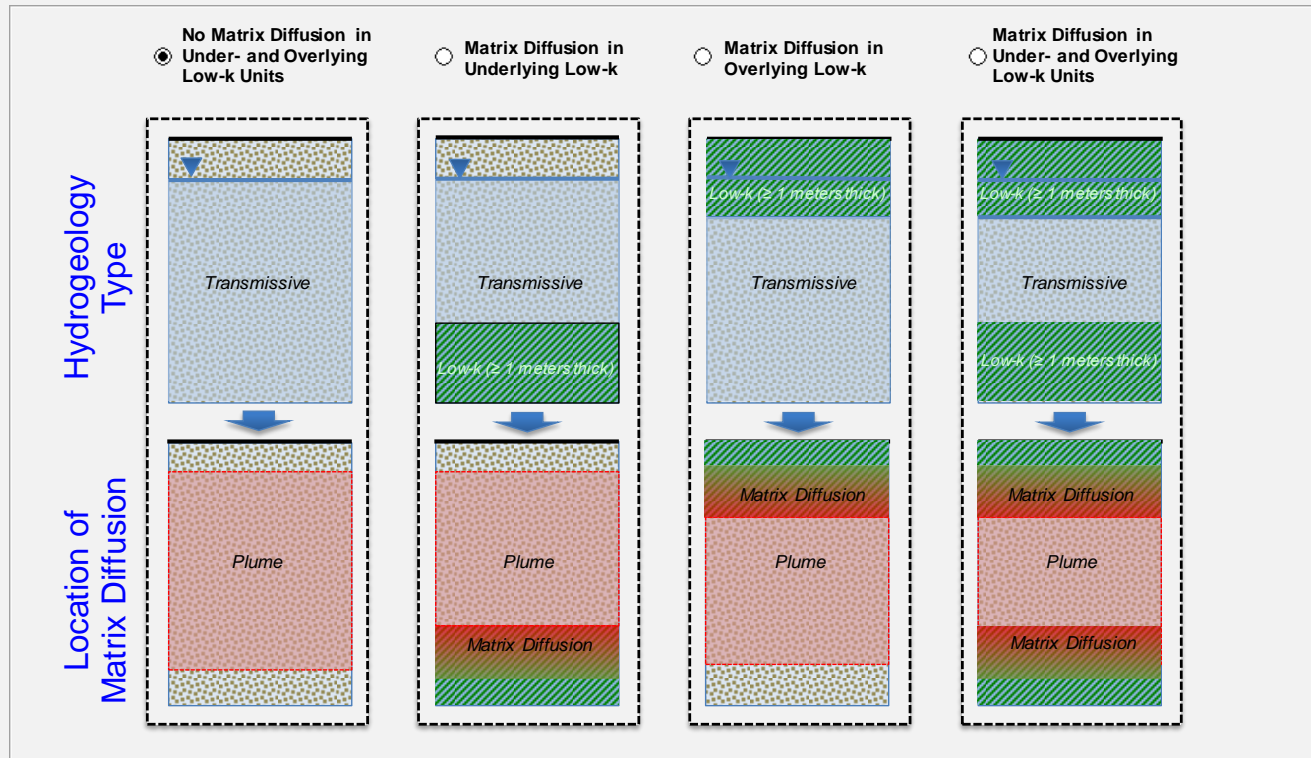
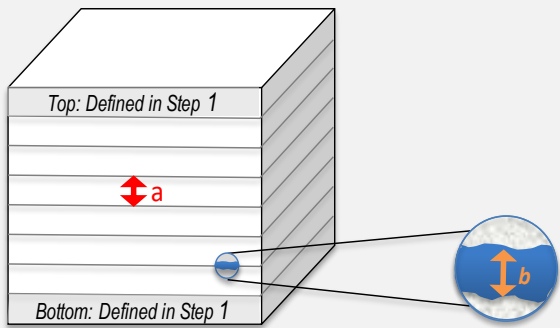


Figure 2.2. REMChlor-MD heterogeneity input parameters – location of matrix diffusion.

REMChlor-MD Heterogeneity Calculator - Fractured Rock/Media
Version 1.0 Beta



The diagram shows a 3D block of fractured rock. The top and bottom surfaces are labeled 'Top: Defined in Step 1' and 'Bottom: Defined in Step 1' respectively. A red double-headed arrow labeled 'a' indicates the distance between two parallel fractures. A blue double-headed arrow labeled 'b' indicates the thickness of a fracture, shown in a circular inset.

Next:
Continue

Return to
Step 1

Return to Main
Input Screen

Clear Data

HELP

STEP2. Enter Fracture Data

| | |
|--|--------------|
| 1. Typical distance between parallel fractures ("a") | 1.42E+00 (m) |
| 2. Typical thickness of aperture/fracture ("b") | 1.40E-04 (m) |

Figure 2.3. REMChlor-MD heterogeneity input parameters – fracture properties.

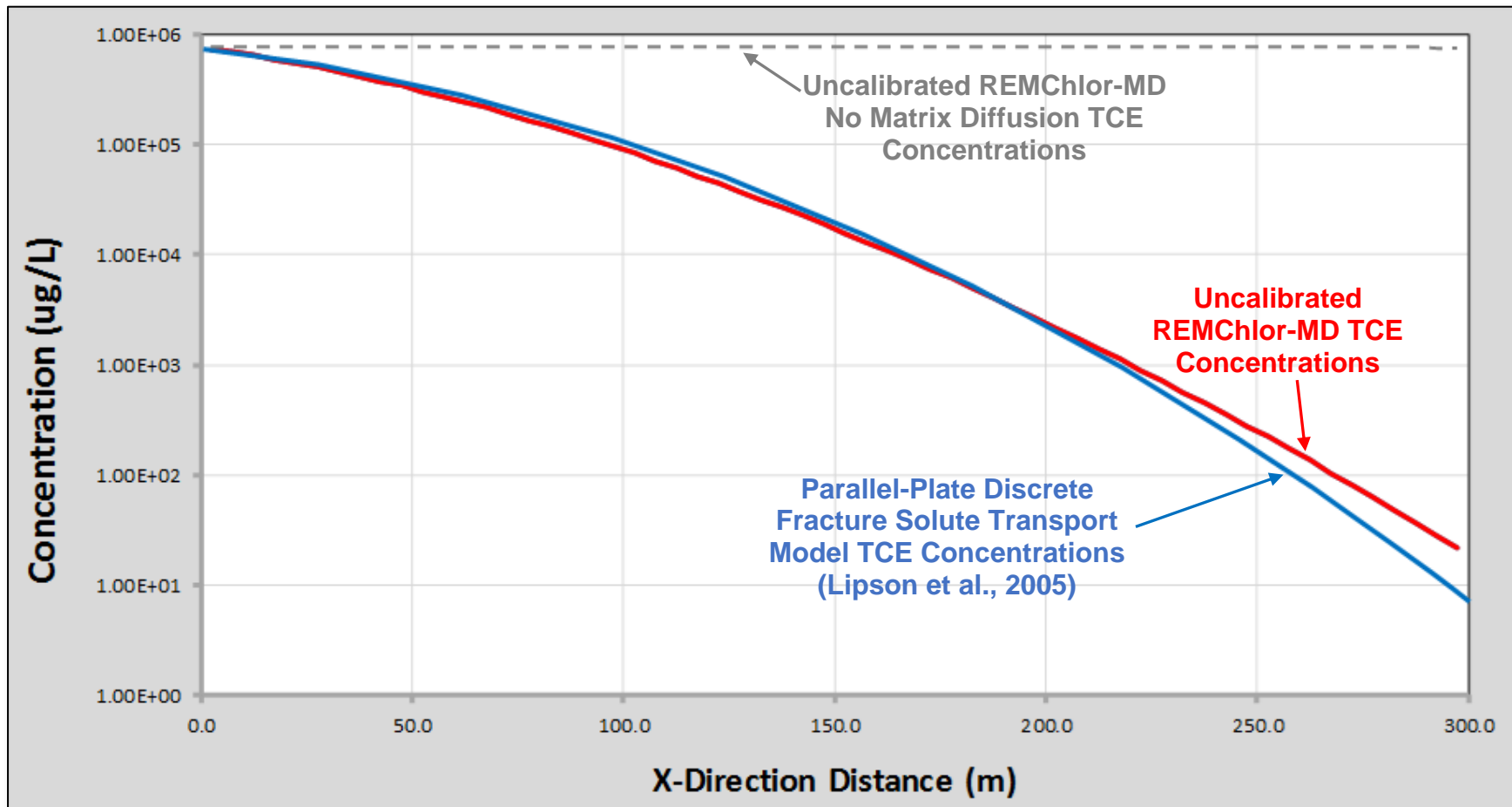


Figure 2.4. Comparison of REMChlor-MD Output (red line) against model output from Lipson *et al.* (2005) (blue line) at 40 years (year 1991) after the source became active. The overall shape of the uncalibrated REMChlor-MD model results matched Lipson *et al.*'s closely and shows an attenuating plume over the first 300 meters downgradient of the source, all due to matrix diffusion (there is no biodegradation in the plume and dispersion is minimal, but TCE is lost to the matrix due to diffusion). The thin dashed gray line displays the REMChlor-MD simulation with matrix diffusion turned off and shows a non-attenuating plume throughout the first 300 meters.

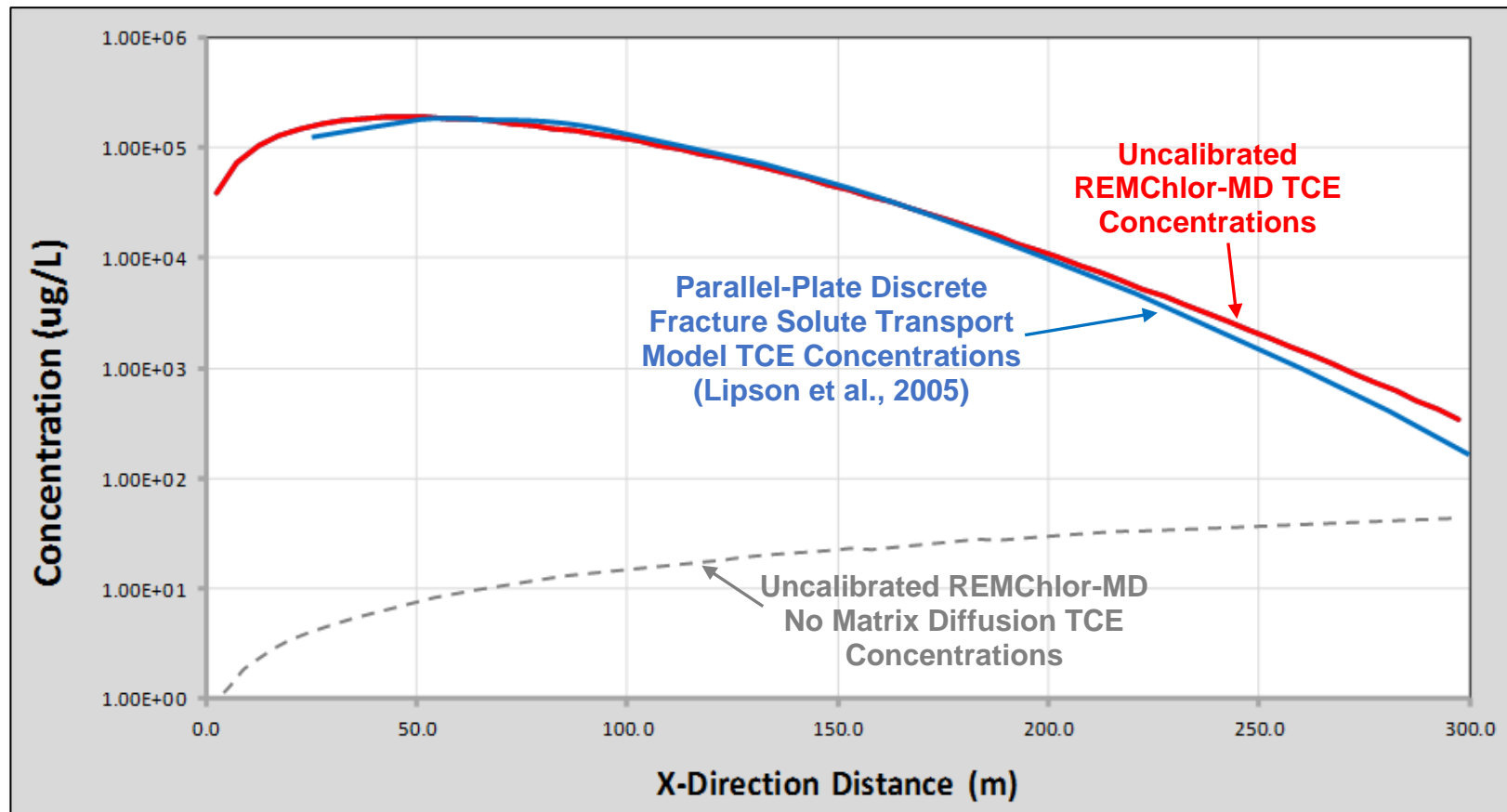


Figure 2.5. Comparison of REMChlor-MD output (red line) against model output from Lipson *et al.* (2005) (blue line) at 60 years after the source became active and 20 years after assumed complete source remediation (i.e., there has been 20 years of clean water flushing through the fractures). The overall shape of the uncalibrated REMChlor-MD model results matched Lipson *et al.*'s closely and shows reductions in concentrations in the first 100 meters compared to Figure 2.4, but higher concentrations 100 to 200 meters downgradient of the source. The thin dashed gray line shows the REMChlor-MD simulation with matrix diffusion turned off and greatly overestimates the degree of plume cleanup due to the source remediation.

CASE STUDY 3. NAS JACKSONVILLE, FLORIDA, BUILDING 780

Overview:

REMChlor-MD was used to demonstrate the estimation of heterogeneity based on high-resolution sampling of low-k zones at the Building 780 area in Operable Unit 3 (OU3) at Naval Air Station (NAS) Jacksonville, Florida. The high-resolution data was obtained by GSI Environmental and the University of Guelph as part of an ESTCP-sponsored project (ESTCP ER-201032).

This building housed a paint stripping and solvent recycling operation and currently is used as a general (non-hazardous) recycling facility and is located in the northern portion of OU3. The exact start date for solvent use is unknown, but it reportedly occurred throughout the 1970s and 1980s to strip paints from aircraft and parts (as well as disposal of spent jet fuels). Chlorinated solvents such as TCE and 1,1,1-TCA have been detected in the soil and groundwater beneath the site, including in a lower permeability clay layer that is present within the sandy shallow aquifer. In the 1990s, remediation efforts (excavation and SVE) were implemented at Building 780 to address contamination associated with this source.

REMChlor-MD was applied as follows:

- Step 1: Values of all parameters, site-specific or Toolkit default parameters, were entered into the model.
- Step 2. Heterogeneity at the site was estimated based on logs from three wells with high-resolution sampling data.
- Step 3. REMChlor-MD outputs were compared to trichloroethene (TCE) and its degradation product groundwater concentrations at two locations, OU3-9 near the source and OU3-11 downgradient from the source. Comparisons were made between the REMChlor-MD simulated outputs and groundwater concentrations obtained using the Source History Tool as documented in Adamson *et al.*, 2015, Farhat *et al.*, 2013, and Newell *et al.*, 2013.

CASE STUDY 3: NAS JACKSONVILLE, FLORIDA
BUILDING 780

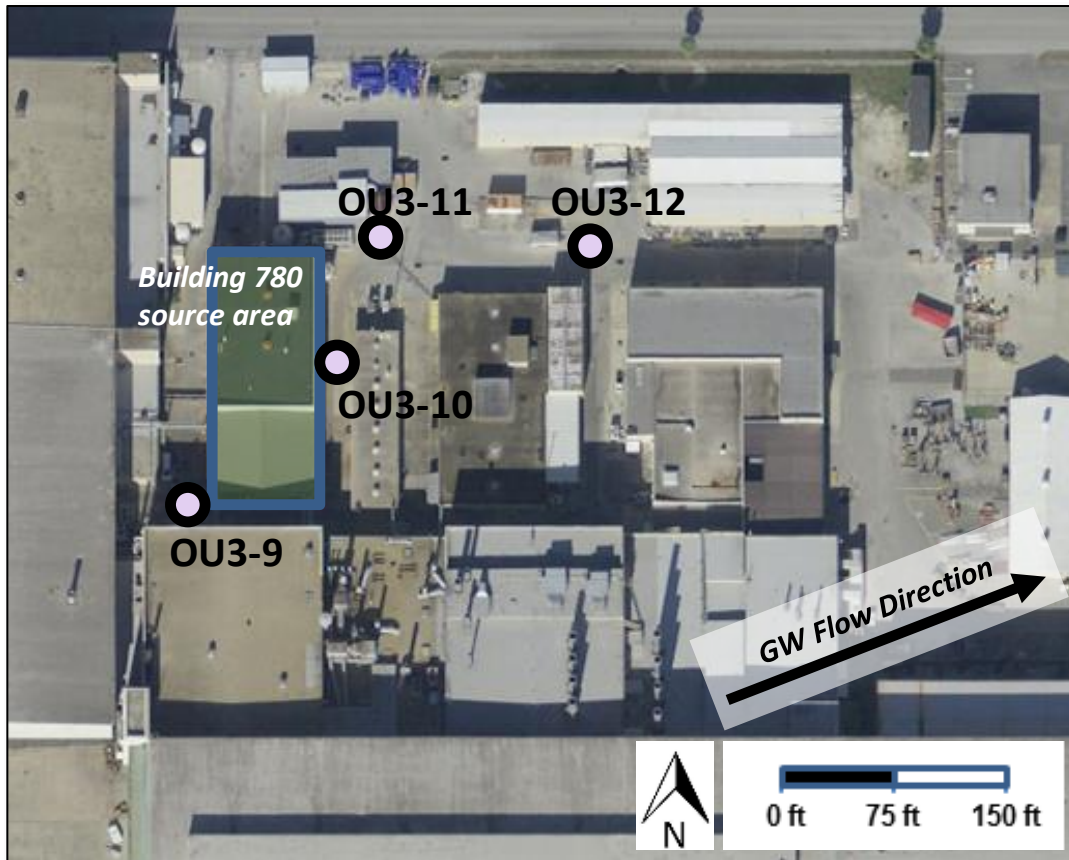


Figure 3.1. Site location map. From Farhat *et al.* (2013) Figure 2.1.

Input Data:

| Data Type | Parameter | Value | Source of Data |
|-----------------------|--|---|---|
| Model Configuration | <ul style="list-style-type: none"> X-direction model size: Y-direction model size: Z-direction model size: Obs. well X-value: Obs. well Y-value: Obs. well Z-value top: Obs. well Z-value bottom: Starting year of simulation: Ending year of simulation: | <ul style="list-style-type: none"> 180 (ft) 150 (ft) 25 (ft) OU3-9: 0 (ft) OU3-11: 180 (ft) OU3-9: 0 (ft) OU3-11: 18 (ft) (initial) OU3-11: 40 (ft) (final) 1 (ft) 0 (ft) 1971 2009 | <ul style="list-style-type: none"> Based on site information (e.g., Newell <i>et al.</i>, 2013; Farhat <i>et al.</i>, 2013; Adamson <i>et al.</i>, 2015) Based on site information Based on site information Assumed 1-ft screen to estimate concentrations close to the T-zone/low-k zone interface Earliest date of solvent use n/a |
| Media Characteristics | <ul style="list-style-type: none"> Transmissive zone: T-Zone K: T-Zone porosity: | <ul style="list-style-type: none"> Sand 20 (ft/d) 0.25 (-) | <ul style="list-style-type: none"> Site information Based on site information Literature (Toolkit default) |

CASE STUDY 3: NAS JACKSONVILLE, FLORIDA BUILDING 780

| Data Type | Parameter | Value | Source of Data |
|------------------------------|---|--|--|
| | <ul style="list-style-type: none"> • T-Zone tortuosity: • Low-k zone: • Low-k K: • Low-k porosity: • Low-k tortuosity: • T-Zone hydraulic gradient: | 0.53 (-) Clay 6.15E-5 (ft/d) 0.38 (-) 0.32 (-) 0.003 (-) | <ul style="list-style-type: none"> • Literature (Toolkit default) • Site information • Literature (Toolkit default) • Site information • Literature (Toolkit default) • Site information |
| Heterogeneity | <ul style="list-style-type: none"> • Top/bottom plume conditions: • Heterogeneity parameters: | No assumed matrix diffusion in under- and overlying low-k units Entered stratigraphic data directly from three boring logs: OU3-9, OU3-10, and OU3-11 | <ul style="list-style-type: none"> • Site information • Site information |
| Contaminants and Source Term | <ul style="list-style-type: none"> • Key constituents: • Initial source concentration: • Source mass: • T-Zone retardation factor: • Low-k zone bulk density: • Low-k. zone fraction organic carbon: • Source Width: • Source Z-value top: • Source Z-value bot: • Molecular diffusion coefficient: | TCE; cis-1,2-DCE; and vinyl chloride TCE: 40 (mg/L) cis-1,2-DCE: 60 (mg/L) Vinyl chloride: 60 (mg/L) All constituents: 1000 (kg) All constituents: 1.7 (-) 1.5 (g/mL) 0.0018 (-) 75 (ft) 25 (ft) 0 (ft) 9.1E-6 (cm ² /sec) | <ul style="list-style-type: none"> • Site information • Assumed • Assumed • Site information • Site information • Site information • Assumed • Assumed • Literature (Toolkit default) • Literature (Toolkit default) |
| Plume Degradation | <ul style="list-style-type: none"> • T-Zone half-life: • Low-k zone half-life: | All constituents: 5 (yrs) All constituents: 1000 (yr) | <ul style="list-style-type: none"> • Assumed • Estimated site information |
| Plume Transport | <ul style="list-style-type: none"> • Longitudinal dispersivity: • Transverse dispersivity: • Vertical dispersivity: | 0 (m) 0 (m) 0 (m) | <ul style="list-style-type: none"> • Assumed • Assumed • Assumed |
| Source Zone Remediation | <ul style="list-style-type: none"> • Percent mass removed: • Year remediation started: • Year remediation ended: • Gamma • Source decay: | 90 (%) 1990 1991 0 (-) 0 (1/yr) | <ul style="list-style-type: none"> • Assumed • Site information • Assumed • Assumed source acting as step function • Assumed |
| Modeling Parameters | <ul style="list-style-type: none"> • Timestep size: • Number of iterations: • Convergence tolerance: • See Results every: | 1 (yr) 500 (-) 1.0E-5 (mg/L) 1 (yr) | <ul style="list-style-type: none"> • Assumed • Toolkit default • Toolkit default • n/a |

Summary:

- REMChlor was used to estimate the sum of TCE, cis-1,2-DCE, and vinyl chloride concentrations due to matrix diffusion after partial source remediation. Input parameters are shown on Figure 3.1 through 3.3 and model outputs on Figures 3.4 through 3.6.
- Site specific boring logs were used to estimate site heterogeneity.

- Model configuration information was entered in Section 2, media characteristics in Section 3, heterogeneity data in Section 4, contaminants and source information in Section 5, plume degradation data in Section 6, plume transport parameters in Section 7, source zone remediation information in Section 8, and modeling parameters in Section 9.
- Where available, site-specific values were used for input parameters.
- The REMChlor-MD model was not calibrated.

KEY POINTS:

The purpose of this evaluation was to demonstrate the use of well logs for estimating site heterogeneity.

REMChlor-MD was able to reproduce total SVOC concentrations reasonably well at both OU3-9 (near source) and OU3-11 (downgradient of source) locations. Simulated concentrations were within an order of magnitude.

The initial y-value location of the downgradient well was unable to reproduce the concentrations in well OU3-11. A better comparison was obtained by increasing the offset of the well from the plume centerline.

References

Adamson, D.T., S.W. Chapman, S.K. Farhat, B.L. Parker, P. deBlanc, and, C.J. Newell, 2015. Matrix Diffusion-Derived Plume Attenuation in Fractured Rock, *Groundwater Monitoring and Remediation*: 1-18.

Farhat, S.K., P.C. deBlanc, C.J. Newell, and D.T. Adamson. 2013. Source History Tool: User's Manual. Prepared for the Environmental Security Technology Certification Program (ESTCP). Project ER-20132.

Newell, C.J., Adamson, D.T., B.L. Parker, S.W. Chapman, and, T. Sale, 2013. Determining Source Attenuation History to Support Closure by Natural Attenuation. Final Report Prepared for the Environmental Security Technology Certification Program (ESTCP). Project ER-20132.

CASE STUDY 3: JACKSONVILLE, FLORIDA BUILDING 780

REMChlor-MD Data Input Screen

Version 1.0 Beta

Site Location and ID:

1. STARTING INFORMATION SI Units English Units Unconsolidated Fractured Rock/Media

2. MODEL CONFIGURATION

Cell Size: X-Direction 1, Y-Direction 2, Z-Direction 1

Model Size: X-Direction 180 (ft), Y-Direction 150 (ft), Z-Direction 25 (ft)

Observation Well Location: X-Value 180.0 (ft), Y-Value 40.0 (ft)

Obs. Well Z-Value Top of Screen 10.0 (ft), Bottom of Screen 0.0 (ft)

Starting Year of Simulation 1971, Ending Year of Simulation 2009

3. MEDIA CHARACTERISTICS

Soil Type: Sand

Transmissive Zone (T-Zone) Sand, Low Permeability Zone (Low-k) Clay

Hydr. Cond. 2.00E+01, Porosity 0.25, Tortuosity 0.53

4. MATRIX DIFFUSION

Calculate Heterogeneity

Average Darcy Velocity 1.14E+01 (ft/yr), Transmissive Zone Volume Fraction 5.19E+01 (%), Average Diffusion Length 3.50E+00 (ft), Surface Area of Low-k Interfaces 2.75E-01 (ft2)

5. CONTAMINANTS AND SOURCE TERM

| Parent | Deg. Prod. 1 | Deg. Prod. 2 | Deg. Prod. 3 |
|---|--------------|----------------|--------------|
| Constituent: TCE | cis-DCE | Vinyl chloride | |
| Initial Source Concentration: 4.00E+01 | 6.00E+01 | 6.00E+01 | |
| Source Mass at Time of Release: 1.00E+03 | 1.00E+03 | 1.00E+03 | |
| Retardation Factor in T-Zone: 1.7 | 1.7 | 1.7 | |
| Retardation Factor in Low-k: 3.4 | 3.4 | 3.4 | |
| Source Width: 75 (ft) | | | |
| Z-Value for Top of Source: 25 (ft) | | | |
| Z-Value for Bottom of Source: 0 (ft) | | | |
| General Molecular Diffusion Coefficient: 9.10E-06 (cm2/sec) | | | |

6. PLUME DEGRADATION

6.1. Degradation First Order Decay Rates

| Distance From Source | TCE | cis-DCE | Vinyl chloride | Component 4 |
|----------------------|------------------|------------------|------------------|---------------|
| Zone 1 | | Zone 2 | Zone 3 | |
| Decay Rate (1,3) | 1.39E-01 | Decay Rate (2,3) | Decay Rate (3,3) | |
| 1.39E-01 | 1.39E-01 | 1.39E-01 | 1.39E-01 | T-Zone (1/yr) |
| 6.93E-04 | 6.93E-04 | 6.93E-04 | 6.93E-04 | Low-k (1/yr) |
| Decay Rate (1,2) | Decay Rate (2,2) | Decay Rate (3,2) | | |
| 1.39E-01 | 1.39E-01 | 1.39E-01 | | T-Zone (1/yr) |
| 6.93E-04 | 6.93E-04 | 6.93E-04 | | Low-k (1/yr) |
| Decay Rate (1,1) | Decay Rate (2,1) | Decay Rate (3,1) | | |
| 1.39E-01 | 1.39E-01 | 1.39E-01 | | T-Zone (1/yr) |
| 6.93E-04 | 6.93E-04 | 6.93E-04 | | Low-k (1/yr) |

6.2. Time Periods

Time Period 2 (T2): 2000 (YYYY year)

Time Period 1 (T1): 1976 (YYYY year)

6.3. Plume Transport

Dispersivity (ft): Longitudinal 0, Transverse 0, Vertical 0

7. SOURCE ZONE REMEDIATION

Percent Source Mass Removed by Remediation: 90 (%)

Remediation Started in Year: 1990 (YYYY year)

Remediation Ended in Year: 1991 (YYYY year)

Mass-Flux/Remaining-Mass Term (Gamma, Γ): 1 (-)

Natural Source Decay Rate: 0 (1/yr)

8. MODELING PARAMETERS

Timestep Size: 1 (yr)

Maximum Number of Iterations: 500 (-)

Convergence Tolerance: 1.00E-05 (mg/L)

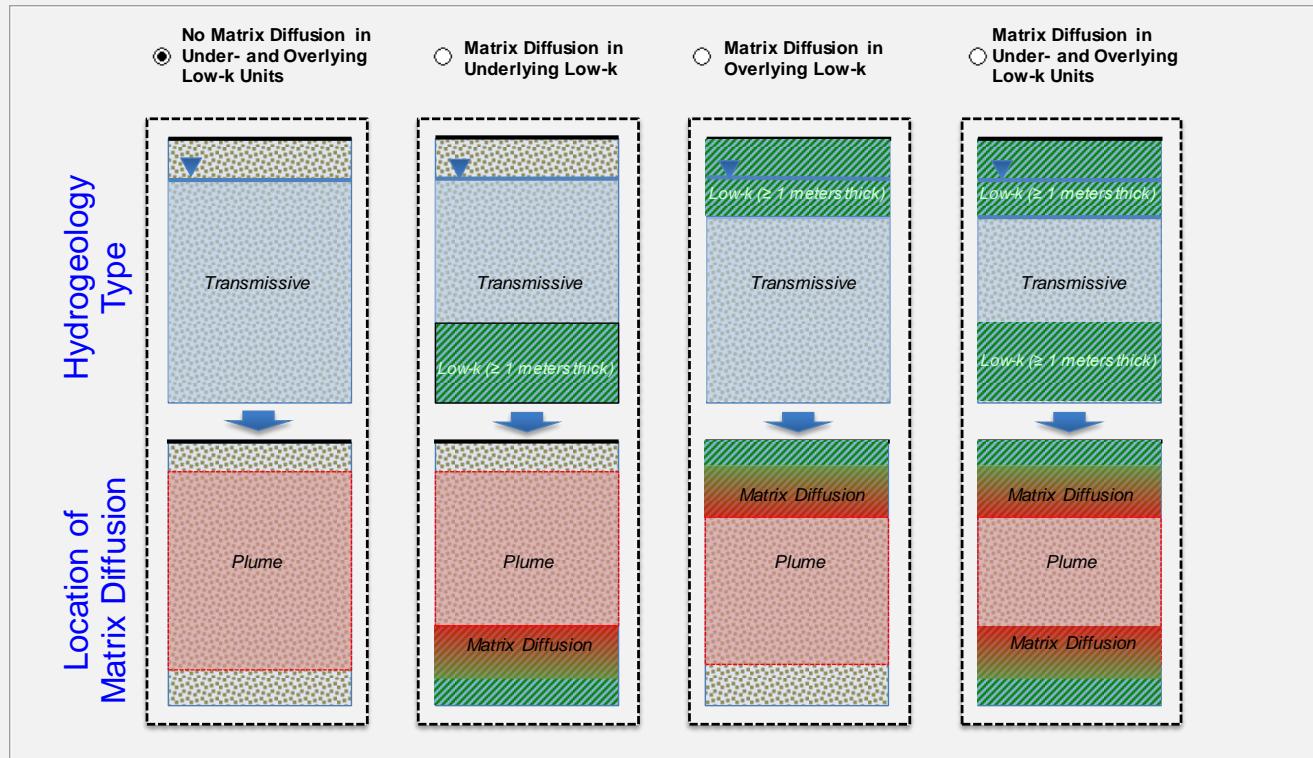
See Results Every: 1 (yr)

Figure 3.1. REMChlor-MD input parameters.

REMChlor-MD Heterogeneity Calculator - Unconsolidated Media

Version 1.0 Beta

STEP 1. Pick One of These Three Basic Top/Bottom Conditions for Your Plume



Next:
Go to Step 2


Return to Main
Input Screen

HELP

Figure 3.2. REMChlor-MD input parameters – location of matrix diffusion.

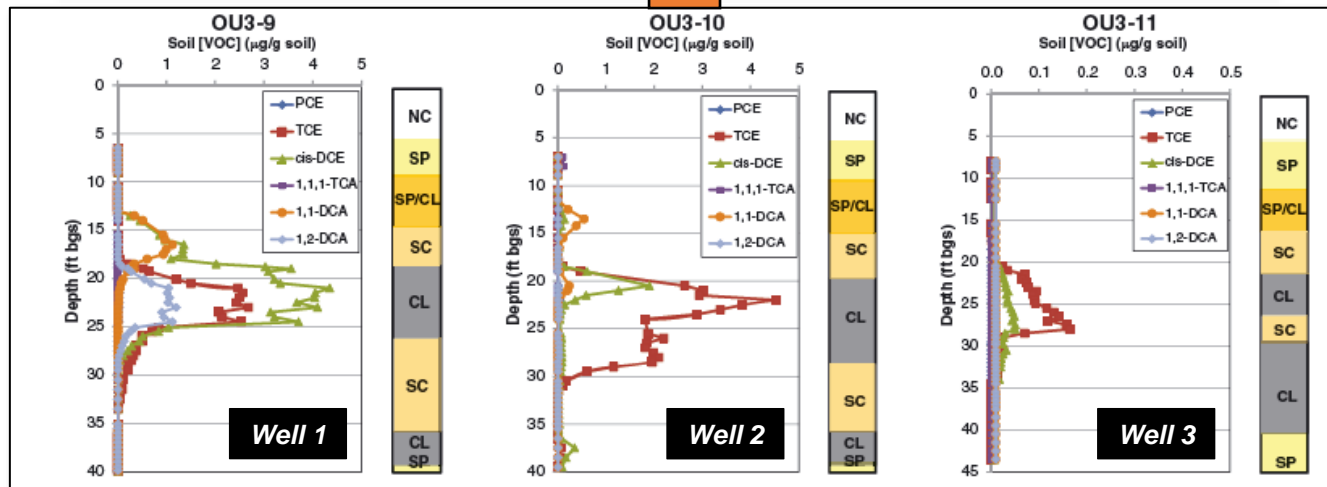
REMChlor-MD Heterogeneity Calculator - Unconsolidated Media Version 1.0 Beta

STEP 3. Estimate Site-Specific Heterogeneity Parameters



- Number of wells to be used (≤ 100 wells)
- Enter the top and bottom of the plume and the thickness for each separate low-k unit. Leave blank if you have entered data for all the low-k units in the boring log.

| | Plume Top (ft bgs) | Plume Bottom (ft bgs) | Low-k Unit Thickness (ft) | | | | | | | | | | | | |
|--------|--------------------|-----------------------|---------------------------|------|---|---|---|---|---|---|---|----|--|--|--|
| | | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | | | |
| Well 1 | 14.00 | 35.00 | 8.00 | | | | | | | | | | | | |
| Well 2 | 13.00 | 31.00 | 8.00 | | | | | | | | | | | | |
| Well 3 | 20.00 | 35.00 | 5.00 | 5.00 | | | | | | | | | | | |



(Notes:
 SP = sand;
 SC = clayey sands;
 CL = clay;
 NC = no core.)

Figure 3.3. REMChlor-MD input parameters – estimation of heterogeneity based on well logs. Bottom panel from Adamson *et al.*, 2015.

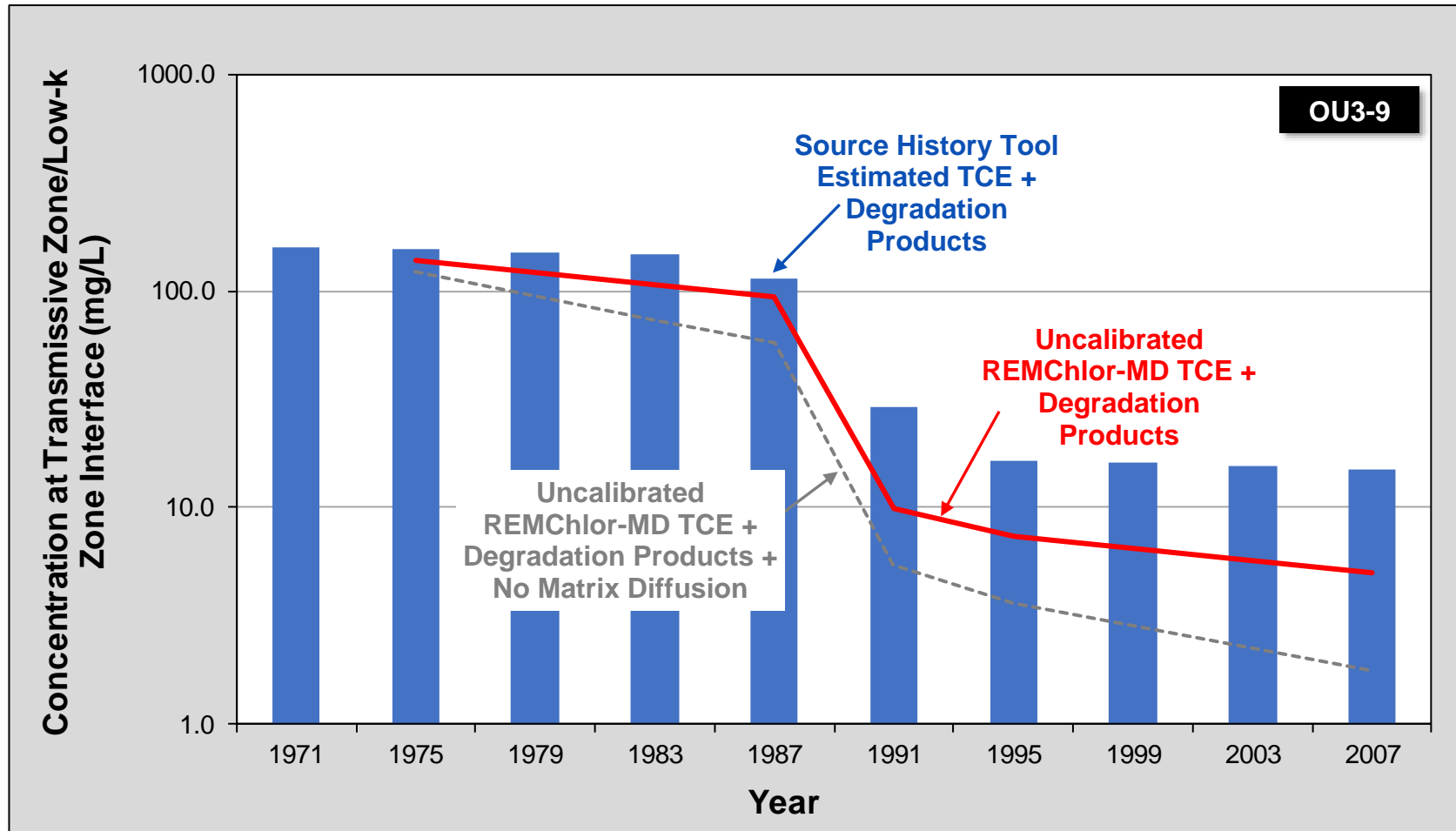


Figure 3.4. Comparison of REMChlor-MD (red line) and Source History Tool (blue bars) simulated concentrations versus time at location OU3-9. (Note there were no actual monitoring wells extending back to 1970; the blue bars are estimated concentrations from the Source History Tool modeling. REMChlor-MD provided a good match, one that is much better than the REMChlor-MD simulation without matrix diffusion (dashed gray line). See Adamson *et al.*, 2015, Farhat *et al.*, 2013, and Newell *et al.*, 2013 for details on the Source History Tool.

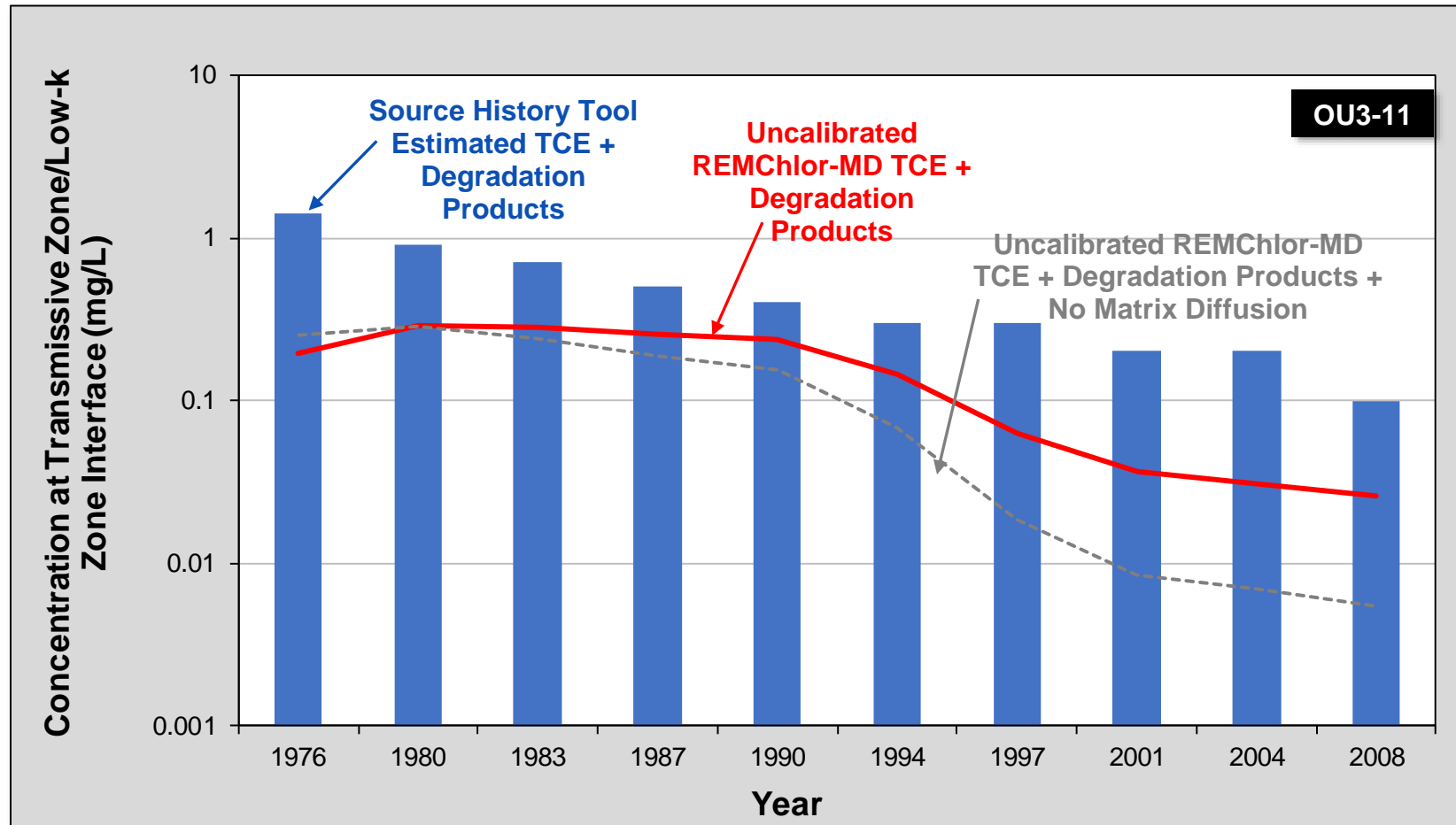


Figure 3.5. Comparison of REMChlor-MD (red line) and Source History Tool (blue bars) simulated concentrations versus time at location OU3-11. (Note there were no actual monitoring wells extending back to 1970; the blue bars are estimated concentrations from the Source History Tool modeling.) REMChlor-MD provided a more accurate match compared to a REMChlor-MD simulation without matrix diffusion (dashed gray line). See Adamson *et al.*, 2015, Farhat *et al.*, 2013, and Newell *et al.*, 2013 for details on the Source History Tool. The match at this location was not as good as shown in Figure 3.4, but does show the matrix diffusion run (red line) provides a better match than the non matrix diffusion run (thin dashed line).



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