Using REMChlor-MD to Assess the Impact of Matrix Diffusion on Chlorinated Solvent Sites

April 2024

Introduction

Remediation of chlorinated solvent plumes is a difficult technical challenge, as complete restoration of the groundwater back to original conditions has been demonstrated at only a few sites. This fact sheet summarizes a key factor responsible for this difficulty - matrix diffusion. Matrix diffusion is the process by which contaminants in groundwater initially migrate from areas of higher concentration in high-permeability zones (e.g., sands and gravels) into low-permeability media (e.g., clayey sands, silts, and clays). When the groundwater plume concentrations in the high-permeability zones are reduced, this diffusion process can occur in reverse ("back-diffusion") and can serve as a difficult-to-manage secondary source long after the primary contaminant source has been removed or controlled.

Figure 1. Launch screen for REMChlor-MD groundwater remediation model (Courtesy of ESTCP)

REMChlor-MD Model Background

REMChlor-MD is an important advancement in the field of groundwater remediation modeling (Figure 1). The model was developed under Environmental Security Technology Certification Program (ESTCP) Project No. ER-201426 with the goal of accurately simulating the fate and transport of chlorinated solvents in groundwater, while taking into account the complex effects of matrix diffusion, including forward and back-diffusion processes (Falta et al., 2018). The model can simulate advection, dispersion, sorption, and reductive dechlorination processes in heterogeneous aquifers and aquitards and in layered systems where aquifers and aquitards are interbedded.

By more accurately simulating the complex effects of matrix diffusion, the REMChlor-MD model allows for more effective planning and execution of remedial approaches, helping to tackle persistent challenges in restoring and managing contaminated groundwater.

REMChlor-MD Model Considerations

Key considerations for the application of the REMChlor-MD model are as follows:

- REMChlor-MD models can be developed by experienced groundwater fate-and-transport personnel in a few weeks using data from existing site characterization efforts.
- After site hydrogeologic, source, chemical, and transport data are entered into the model, parameters can be adjusted to generally match: 1) the source concentration versus time data (if available); and 2) the plume centerline concentrations versus distance from the source.
- After calibration, the REMChlor-MD model can be used to answer questions, such as:
  - Is matrix diffusion an important part of the conceptual site model?
  - How much contaminant mass could be trapped in low-permeability geologic media?
  - If the source is remediated, will cleanup standards be met without removing contaminants from low-permeability zones?
  - What are realistic expectations for site restoration at a particular site?

Modeling the Effects of Matrix Diffusion at Remediation Sites with REMCHLOR-MD

REMChlor-MD Modeling Approach

To model matrix diffusion using REMChlor-MD, the user first needs to gather and input various data into the model as described below:

1. **Hydrogeologic data:** includes information about the geology and physical characteristics of the aquifer system. Two broad types of water-bearing units can be modeled: unconsolidated formations (e.g., sand, silt, clay) and fractured media (e.g., sedimentary rock, granite, and fractured clays). A geologic heterogeneity calculator is used to include the presence of low-permeability units above or below the transmissive unit. Then, the user enters information about the presence of layers or lenses within the transmissive zone (see Figure 2).
2. **Source data:** includes the type of contaminants that will be simulated, their concentrations, an estimate of the mass released by the source, and the duration and nature of release.
3. **Chemical data:** includes information about the contaminants and their behavior in the subsurface, such as their molecular weight, partition coefficient, and any relevant degradation rates or reaction information, if applicable.
4. **Transport data:** may include measurements of contaminant concentrations at different points and times in the aquifer, which can be used to validate the model results, as well as dispersivity.

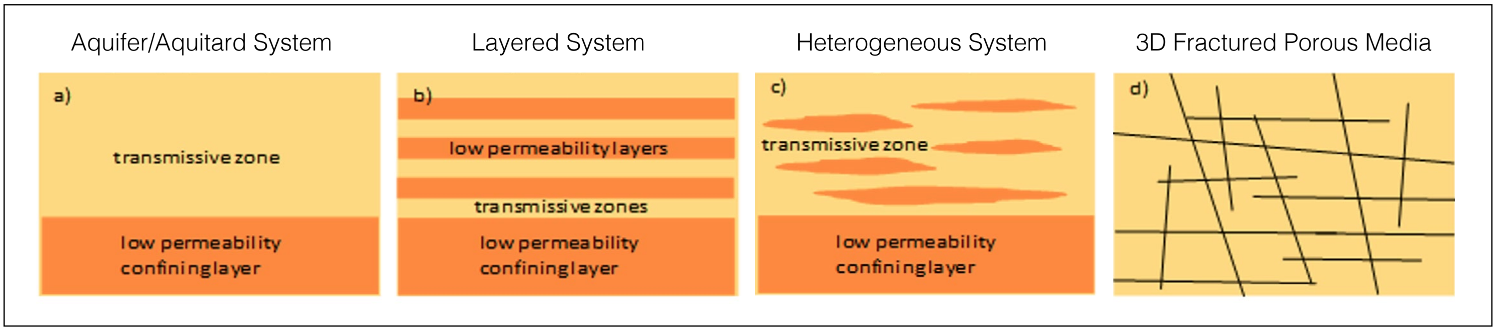

Figure 2. Examples of four different hydrogeologic settings that can be simulated in REMChlor-MD to account for matrix diffusion processes (Courtesy of GSI Environmental, Inc.)

More details on how to use the REMChlor-MD model can be found in these resources:

- REMChlor-MD User's Manual (Farhat et al., 2018)
- Key scientific papers (Falta and Wang, 2017; Muskus and Falta, 2018)
- Strategic Environmental Research and Development Program (SERDP) Transition Assessment Assistant (TA2) Web Tool, Tool 6d (SERDP Project Number ER20-1429)

REMChlor-MD Remediation Case Studies

Two case studies, Naval Air Station North Island (NASNI) and Naval Base Kitsap (NBK) Keyport, are provided as examples of the application of REMChlor-MD at Department of the Navy (DON) Installation Restoration (IR) sites.

REMChlor-MD simulates the fate and transport of chlorinated solvents in groundwater, while taking into account the complex effects of matrix diffusion.

CASE STUDY 1

REMChlor-MD Large Chlorinated Solvent Source Zone

Site Background: NASNI is bounded by San Diego Bay on the west and north and by the Pacific Ocean to the south. From the 1940s through the mid-1970s, NASNI IR Site 9 served as a chemical waste disposal area (DON, 2019). The geology comprises several stratigraphic layers consisting predominantly of clean sands interbedded with silts, silty sands, shell-rich strata, clay, and gravel. Key groundwater constituents of concern were trichloroethene (TCE) and its degradation products (cis-1,2-dichloroethene [cDCE] and vinyl chloride [VC]). The source zone was assumed to have contained dense non-aqueous phase liquid (DNAPL) to a depth of 45 feet across an area measuring about 335 feet by 225 feet (Figure 3).

Key Question: If remediation was implemented in the source zone (e.g., source isolation or source mass removal via an in situ technology), would the long-term site conditions be meaningfully improved versus solely monitored natural attenuation (MNA)?

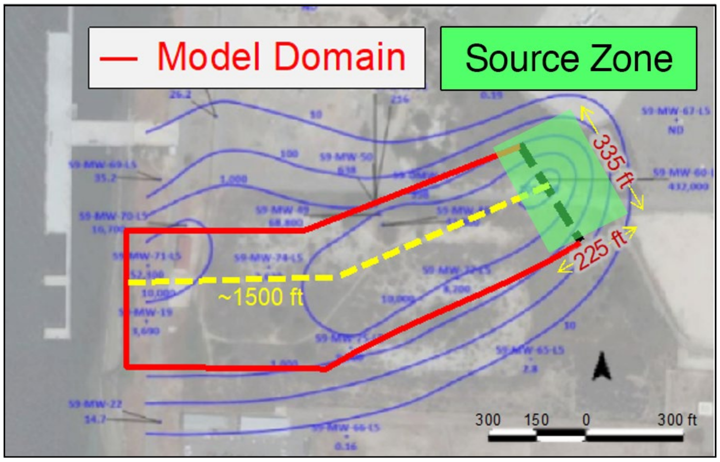

Figure 3. DNAPL source zone and REMChlor-MD model domain for NASNI IR Site 9 (Courtesy of NAVFAC)

Key Modeling Results: REMChlor-MD modeling predicts that active remediation (i.e., source isolation or treatment technology) will have a minimal impact on the long-term persistence of the groundwater plume at this site because matrix diffusion will cause diffuse, widespread sources that maintain elevated groundwater concentrations for decades. Without matrix diffusion (an impossible scenario for this type of hydrogeologic setting), the model shows that isolating the source zone with a slurry wall reduced TCE concentrations at the shoreline to below the cleanup goal (0.081 mg/L) within 25 years of complete source isolation (Year 2050 minus Year 2025). With matrix diffusion, the model shows a remedial timeframe of about 165 years after complete source zone isolation (Year 2190 minus Year 2025). These results further indicate that an in situ source remediation-scenario that was able to remove 90% of the source mass yielded results similar to the source isolation-scenario (Figure 4). For the MNA-only scenario, source concentrations, source mass, and other model parameters were adjusted during calibration to match observed 2020 plume concentrations at the source and shoreline monitoring wells. With matrix diffusion and no source remediation, the MNA-only scenario in Figure 4 shows a remedial timeframe of about 230 years (Year 2250 minus 2020) with REMChlor-MD modeling. Thus, source isolation results in only a 28% decrease in the estimated remedial timeframe.

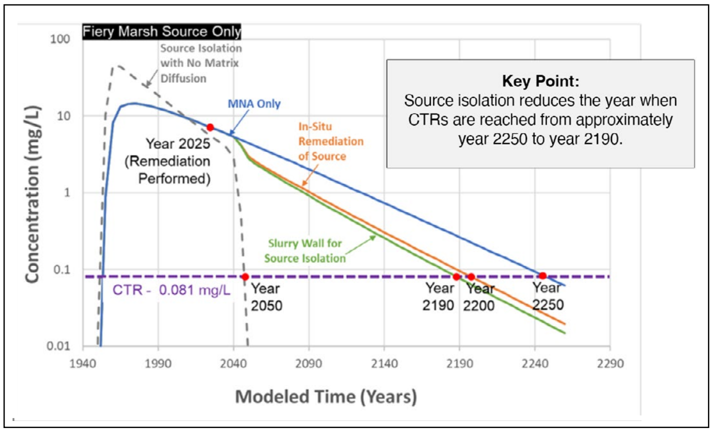

Figure 4. REMChlor-MD forecasted concentration vs. time curves for three remedial scenarios (Courtesy of GSI Environmental Inc.)

Notes:

1) MNA starting in Year 2020 (blue line);

2) 90% source removal in Year 2025 (orange line);

3) Complete source isolation in Year 2025 by a deep slurry wall (green line); and

4) The gray dashed line shows a hypothetical no matrix diffusion case with complete source isolation in Year 2025 and the purple dashed line is the California Toxics Rule (CTR) TCE concentration criteria.

REMChlor-MD modeling results indicated that source isolation would result in only a 28% decrease in the estimated remedial timeframe.

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CASE STUDY 2

REMChlor-MD
Small Chlorinated Solvent Source Zone

Site Background: Keyport Operable Unit (OU) 1 is a former landfill that received wastes from base operations between the 1930s and 1973, when the landfill was closed. Chlorinated solvents and 1,4-dioxane are present in groundwater, with the highest concentrations at several "hotspots." This REMChlor-MD modeling project focused on evaluating fate and transport in the vicinity of the hotspots in OU-1. At Hotspot 1, TCE concentrations of up to 800,000 µg/L were observed (Figure 5). The nearest potential receptor was a stream and marsh located to the south and downgradient of the hotspot.

Key Question: If the hotspot was remediated to reduce the mass flux leaving the source, would the same reduction in source concentration be observed in the downgradient plume?

Key Modeling Results: REMChlor-MD modeling shows that matrix diffusion is an important part of the conceptual site model. If complete source removal/isolation in the Year 2025 is assumed (e.g., complete excavation or isolation with a slurry wall), the model without matrix diffusion indicates that site remedial goals would be met 49 years after source treatment (Year 2069 in Figure 6). However, the model with matrix diffusion indicates that site remedial goals would be met 154 years after source treatment, about 110 years longer (Year 2179 in Figure 6). Similarly, removing 90% of the source mass in the Year 2025 has little impact on the long-term fate and transport of the groundwater plume (Figure 7).

A typical in situ remedial technology (e.g., thermal treatment, chemical reduction, biodegradation, chemical oxidation) can remove about 90% of the source mass and reduce source concentrations by about 90% (McGuire et al., 2016). However, removing 90% of the source mass does not equate to removing 90% of the mass contained in the low-permeability and transmissive zones in the plume downgradient of the source. After source removal or treatment, the mass in the low-permeability zones will continue to "feed" the groundwater plume for centuries, as shown by the REMChlor-MD model. For Hotspot 1, removing 90% of the source mass decreased the remedial timeframe for VC from about 600 years (2626 years minus 2025 years; assuming no remediation) to about 450 years (2477 years minus 2025 years). Thus, source treatment results in only a 25% decrease in the remedial timeframe despite removing 90% of the source mass in the Year 2025 (Figure 7).

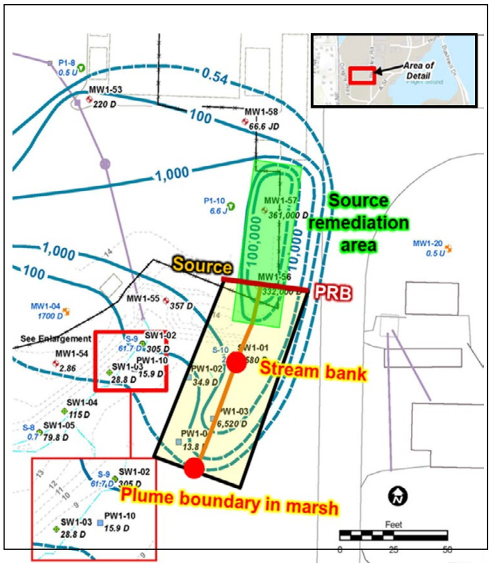

Figure 5. TCE isocontour map of Hotspot 1 at the Keyport OU-1 Site (Courtesy of NAVFAC)

Notes: The source zone is denoted in green and the REMChlor-MD model domain in yellow.

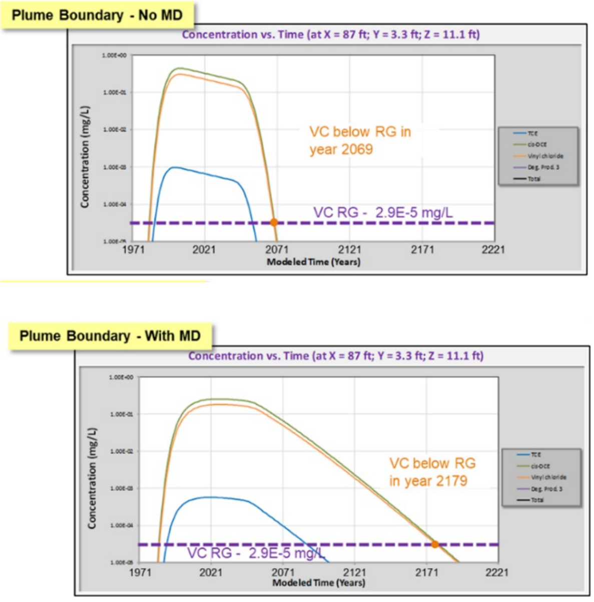

Figure 6. REMChlor-MD forecasted Keyport OU-1 Hotspot 1 concentration vs. time trends with and without matrix diffusion. (Courtesy of GSI Environmental, Inc.)

Notes: Both with 100% complete source removal;
MD = Matrix Diffusion; and RG = Remediation Goal

REMChlor-MD model results indicated that source treatment would result in only a 25% decrease in the remedial timeframe.

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Case Study 2: Continued

Case Study 2: Small Chlorinated Solvent Source Zone (Continued)

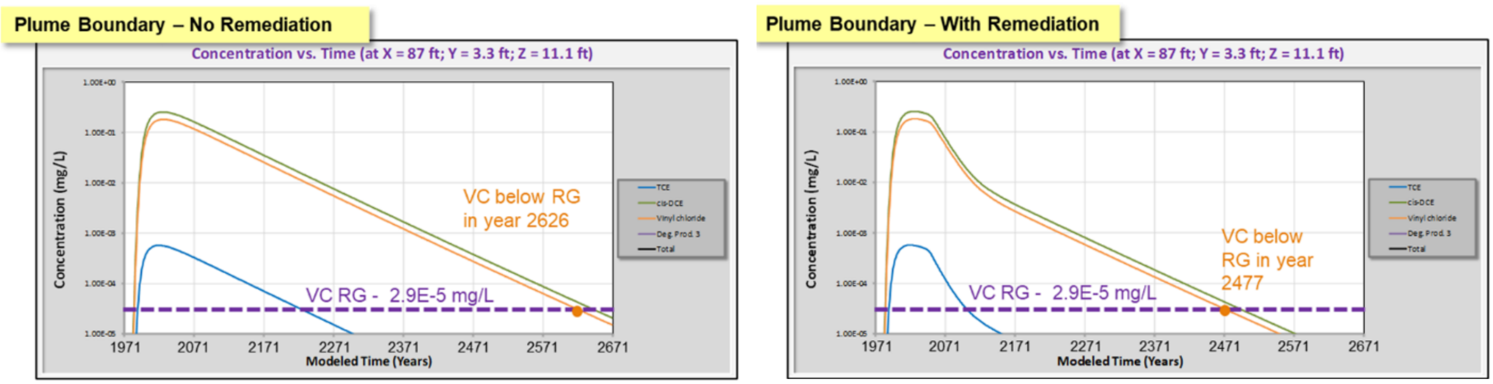

Figure 7. REMChlor-MD forecasted Keyport OU-1 Hotspot 1 concentration vs. time trends with no source remediation vs. 90% source removal (Courtesy of GSI Environmental, Inc.)

Notes: MD = Matrix Diffusion and RG = Remediation Goal

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