Fact Sheet

Performance of Two Technologies to Control Difficult-to-Treat Matrix Diffusion Zones: Post-Bioremediation Sustained Treatment and MNA in Low Permeability Units

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14. ABSTRACT
In-situ bioremediation (ISB) and monitored natural attenuation (MNA) are two widely used approaches to treat and control persistent matrix diffusion sources at chlorinated solvent sites. Such source zones represent a significant liability to the Department of Defense (DoD). Research has suggested that processes may be active at both ISB and MNA sites that could provide additional benefits to their application near or within low-permeability (low-K) matrix diffusion zones. The objectives of the project were: i) to develop new process knowledge on how to measure and demonstrate sustained treatment following application of ISB and ii) to evaluate and quantify MNA processes in low-K matrix diffusion zones. Data from field demonstrations and data mining of other sites indicated the occurrence of these processes and provided useful information on quantifying and assessing these processes. Fact Sheets are provided to allow cost effective application of these concepts at other sites using existing site data.

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Use of Low-K MNA Data in Matrix Diffusion Modeling

ESTCP Project ER-201429

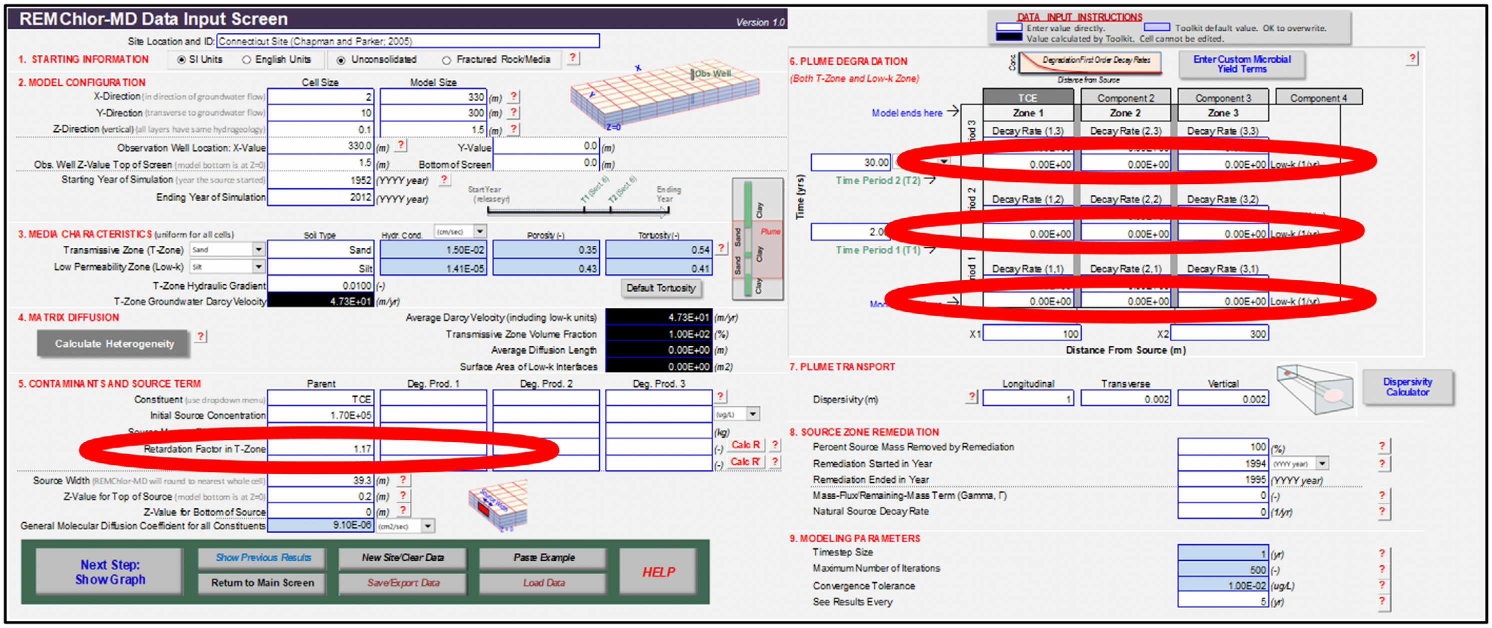
The REMChlor-MD computer model (ESTCP Project ER-201426) provides a practical and efficient mathematical method to account for the effects of matrix diffusion in groundwater transport and remediation. By accounting for contaminant diffusion in and out of heterogeneous settings, including fractured porous media and sites with extensive low permeability layers and lenses, site decisions regarding plume migration and the effectiveness of in situ remediation can now be evaluated. However, some of the input data required to model matrix diffusion is relatively unusual. The data generated as part of the ER-201429 ESTCP Project described in this fact sheet do provide insights on how to build and simulate matrix diffusion at your site.

REMChlor-MD Model

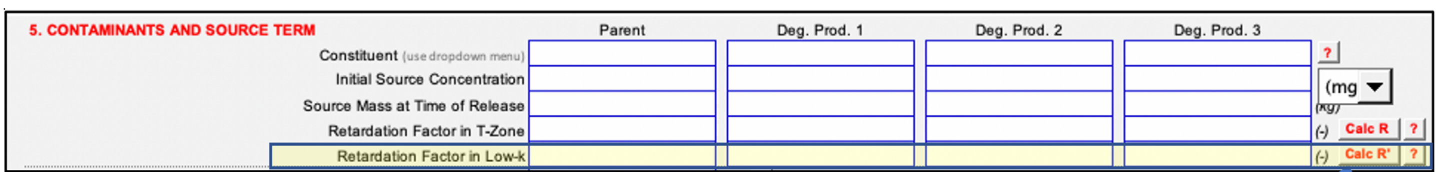
The REMChlor-MD (Falta et al., 2013; Farhat et al., 2018) model introduction screen is shown below. The input screen is also shown below, with red circles showing matrix diffusion input data that are required, but generally new to many groundwater modelers. These key data are presented in more detail on the following pages.

About ESTCP

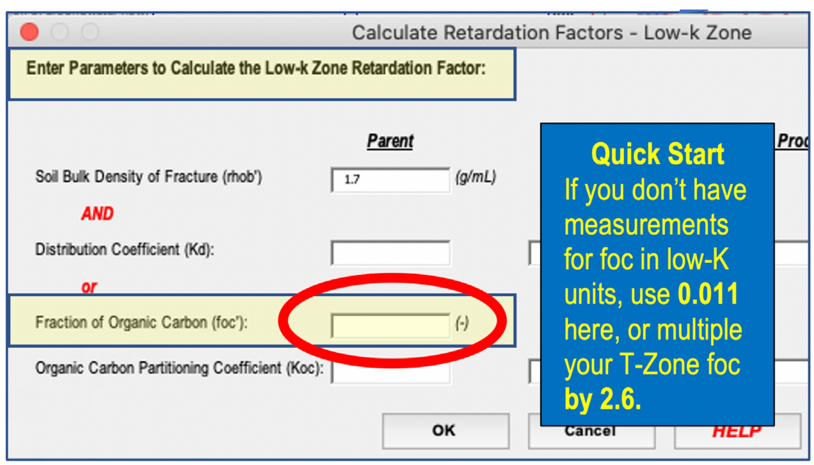
The Environmental Security Technology Certification Program (ESTCP) is the U.S. Department of Defense's environmental technology demonstration and validation program. The program's goal is to identify and assess innovative technologies that address DoD's high-priority environmental requirements efficiently and cost-effectively.



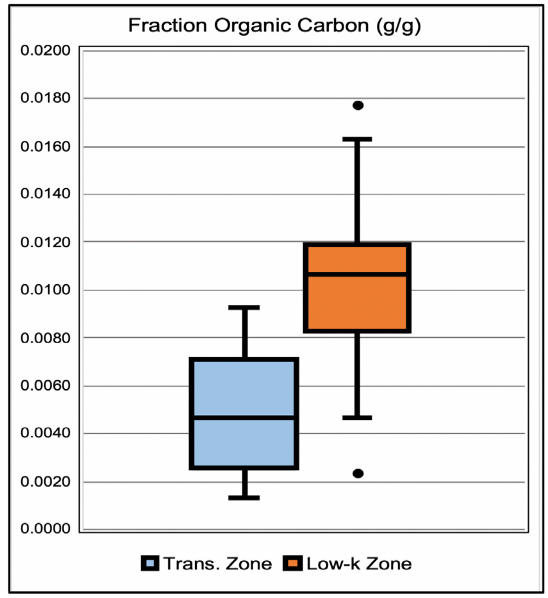
Key Input #1: What is the Retardation Factor of the Low Permeability ("Low-K") Zone?



We often measure the transmissive zone ("T-Zone") geologic media (e.g., sands/ gravels) to determine the fraction organic carbon (foc) to get the retardation factor for a groundwater transport model. In situations where foc data are not available for the transmissive zone, often a value of 0.001 is used as a conservative rule of thumb to run the model (see REMChlor-MD manual). The typical range is reported as 0.0002 - 0.02 for transmissive zones. But measurement of foc in the low-K geologic media (such as silty or clayey media) is not a typical practice. **If these data are not available, what values for foc are appropriate for the low-K units?**



This project collected a total of 18 and 48 samples from transmissive zone and low-K units, respectively (typically 4 transmissive and 16 low-K samples each from England AFB, Hill AFB, and Kelly AFB. As shown in the box plots to the right, the median foc for the aquifer transmissive zone (blue box, right) is 0.0047 grams foc per gram of soil. (The box defines the 75th and 25th percentiles of the samples, the whiskers are the extremes, the median is the horizontal line, and the dots are statistical outliers). The median foc for the 48 low-K samples was **0.011 g/g** (1.1%). The low-K unit foc was about 2.6 times higher than the transmissive zone foc, so if only transmissive zone foc data are available one could **multiply those values by 2.6** to get an estimate for the foc in the low-K zone.



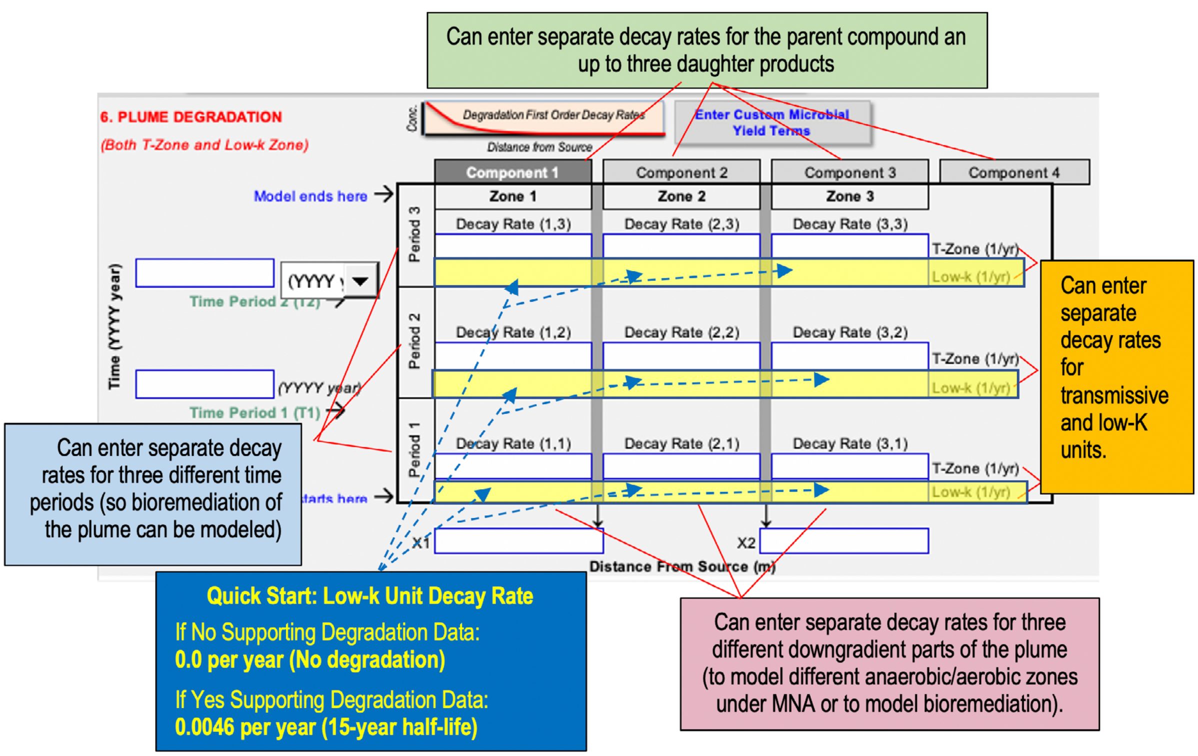
KEY POINT: REMChlor-MD Fraction Organic Carbon (foc) in Low-k Zones

If you don't know foc values to enter in REMChlor-MD, consider using:

- A value of **0.011** grams foc per gram soil (-) for the low-K zones in the model, or
- Multiply your transmissive zone foc **by 2.6** to get a low-K zone foc value.

Key Input #2: What Decay Rates for the Low-K Unit to Use in REMCHLOR-MD?

The ability to put in different decay rates for chlorinated solvents is one of the most powerful but one of the most challenging parts of using REMChlor-MD. One can put in a decay rate (in units of per year) for:



At this stage of the matrix diffusion/chlorinated solvent conceptual model, the decay rate over time is assumed to stay relatively constant so the same values will be used for Period 1, 2, and 3. Similarly, any type of remediation will have relatively little effect on the low-K zones, so the same values will be used for Zones 1, 2, and 3. But what values should be entered into the model? Due to the nascent nature of this topic, the REMChlor-MD manual does not discuss low-K decay rates in any detail, but three case studies assumed no degradation in low-K zones.

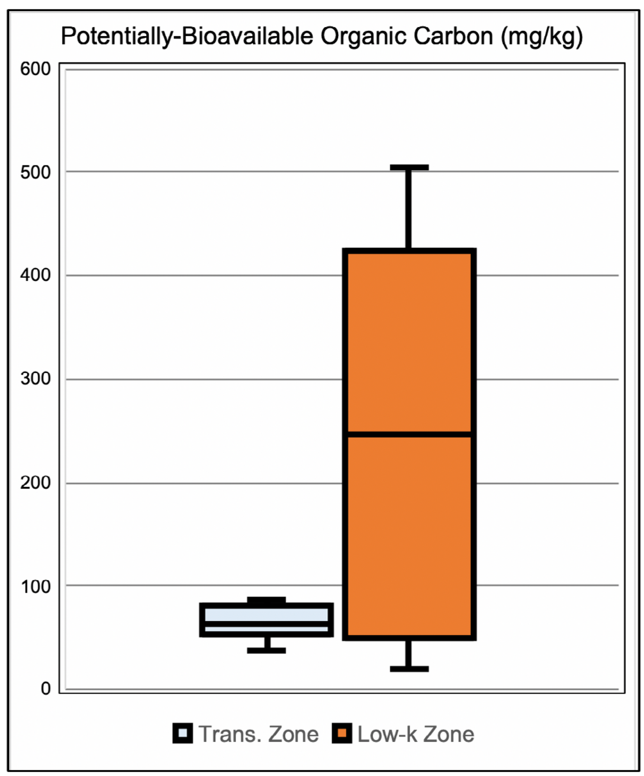
SERDP Project ER-1740 (Sale et al., 2013) provides the state of knowledge about biodegradation of chlorinated solvents in low-K units as of the year 2014. They reported:

In all of the above studies, microorganisms, such as Dehalococcoides, were observed not only within the most porous sections of the subsurface, but well inside geological materials with low permeabilities – i.e., 10's of centimeters or more from an interface with a high permeability zone (Lima et al., 2012a; Lima et al., 2012b; Scheutz et al., 2010; Takeuchi et al., 2011). Microbial numbers were admittedly relatively low, as were the growth rates. Nevertheless, the impact these microbial communities exerted on the distribution of contaminants may have been considerable. Therefore, these populations are likely to play an important role in contaminant natural attenuation, to control rates of back diffusion, and to influence the longevity of plumes sustained by back-diffusion.

Three detailed field studies where low-K zones were evaluated for degradation were discussed:

- Florence, South Carolina: **Strong** Evidence of degradation in low-K zones
- Jacksonville, Florida: **Limited** Evidence of degradation in low-K zones
- CS-10 Plume, Massachusetts: **No** Evidence of degradation in low-K zones

The data generated as part of the ER-201429 ESTCP Project described in the Final Report do provide additional data and interpretations about if and how to model degradation in low-K units via these lines of evidence.



Qualitative Information PBOC: The low-K sample analysis showed that low-K units did have a substantial amount of potentially-available bioavailable organic carbon (PBOC) that could sustain reductive dichlorination reactions in low permeability media such as silts and clays. The median PBOC concentration was **247 mg/kg**, about four times higher than the median value of 64 mg/kg in the transmissive zone geologic media.

Semi-Quantitative Information Source History Modeling: High-resolution low-K zone soil data comprised of closely spaced samples collected vertically within the low-K units were used to compile trichloroethene (TCE) soil concentration vs. penetration depth data in low-K units collected at four different sites to determine if using biodegradation rates within these low-K zones, in the form of first order decay coefficients, made a 1-D diffusion model more accurate. The Source History Tool (Farhat et al., 2013) was used to compare the actual data vs. diffusion model output for low-K clay stratum at two sites at Hill Air Force Base (AFB) and two sites at Kelly AFB.

A reconstruction of the source history based on TCE soil concentrations in the low-K zone, indicated:

- Unclear if degradation was occurring at Location A of Hill AFB.
- Potentially slow degradation **with a half-life of >10 years** was occurring within the low-K unit at Location B of Hill AFB.
- Unclear if degradation was occurring at Location A of Kelly AFB.
- Unclear if degradation was occurring at Location B of Kelly AFB.

Semi-Quantitative Information Data Mining: Multi-year chlorinated ethene concentration vs. time data were compiled from over 500 sites and a total of over 1,500 monitoring wells in the California Geotracker database. Key criteria for inclusion were minimum concentrations of any chlorinated ethene greater than 50 μg/L, at least five years of monitoring data, and at least four monitoring points. Sites were divided into two categories, likely dry cleaner sites and Department of Defense sites (see ER-201429 Final Report).

One relevant analysis was to evaluate the kpoint (first-order decay rate for concentration vs. time rates at any well; Newell et al., 2002) for low concentration wells that were likely dominated by matrix diffusion processes and not high strength source zones. These data show how quickly these likely matrix diffusion sources are decaying when a first-order decay model is applied. The resulting half-lives (and their corresponding first order decay rates) are presented below.

Dataset	**PCE**	**TCE**	***cis*-1,2-DCE**
	First order degradation rate, per year *(First order degradation half-life, years)*		
Presumed Mostly PCE Sites (Dry Cleaners) Site Maximum Concentration < 50 μg/L	0.096 (7.2)	0.052 (13)	0.034 (21)
Presumed Mostly TCE Sites (DOD Facilities) Site Maximum Concentration < 50 μg/L	0.054 (13)	0.046 (15)	0.050 (14)

This analysis shows that these sources decay very slowly, with concentrations falling by 50% every 7 to 20 years. If one assumes that these concentrations are primarily sustained by matrix diffusion sources and no dense non-aqueous phase liquid sources, then the decay within these units is unlikely to be faster than the rates presented in the table above. Therefore, if no site-specific data are available, one could assume that an upper bound degradation half-life is about 15 years (first order decay rate of 0.046 per year). If there is qualitative evidence that some type of decaying is occurring in the low-K zones (via molecular biological tools, isotope analysis, detailed analysis of daughter product generation, abiotic degradation indicators, etc.) then this type of rate could be used in REMChlor-MD.

KEY POINT: REMChlor-MD First Order Decay Rates in Low-K Zones

Absent site-specific first order decay rates to enter into REMChlor-MD, weigh these lines of evidence to come up with values to use in your model:

- Of three sites evaluated as part of SERDP Project ER-1740, one site had Strong Evidence of degradation in low-K units; one Limited Evidence, and one No Evidence.

- All three sites analyzed by this project had PBOC, indicating that many sites may have some type of naturally occurring electron donor that could sustain biodegradation. The presence of PBOC is not confirmatory but is just a "potential" driver of biodegradation in low-K zones.

- When the high resolution concentration vs. vertical penetration depth from four locations at two sites was analyzed with the ESTCP Source History Tool (Farhat et al., 2013), only one site had a strong enough signal to discern a first order decay half-life in the low-K unit. This half-life was greater than 10 years (> 0.0693 per year decay rate).

- When over 1500 monitoring wells with low concentration chlorinated ethene concentration vs. time data were evaluated, it suggested that an appropriate general decay rate to use is about 15 years (0.046 per year decay rate).

- Overall, if you do not have any supporting information that degradation is occurring in low-K zones, assume the degradation rate is zero (enter 0.0 per year in decay rates for low-K media in REM Chlor-MD).

- If you have some qualitative evidence that degradation is occurring in low-K zones (molecular biological tools, isotope analysis, detailed analysis of daughter product generation, abiotic degradation indicator) then use a 30 year half-life (enter 0.023 per year in decay rates for low-K media in REMChlor-MD).

- If you have some quantitative rate data on what low-K degradation rates are, use those values directly in REMChlor-MD in units of per year.

FOR MORE INFORMATION

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