

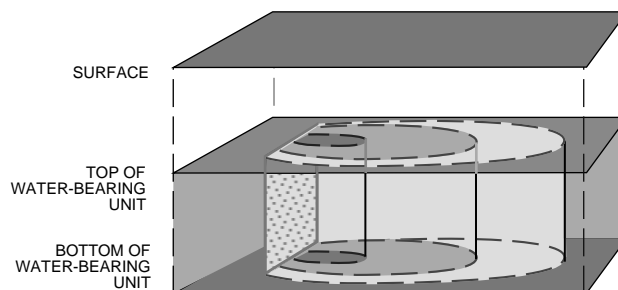
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BIOCHLOR

Natural Attenuation Decision Support System

Version 2.2
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User's Manual Addendum



by

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 Air Force Center for Environmental Excellence Technology Transfer Division

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INTRODUCTION

BIOCHLOR is a screening model that simulates remediation by natural attenuation (RNA) of dissolved solvents in groundwater. The software, programmed in the Microsoft[®] Excel spreadsheet environment and based on the Domenico analytical solute transport model, has the ability to simulate 1-D advection, 3-D dispersion, linear adsorption, and biotransformation via reductive dechlorination (the dominant biotransformation process at most chlorinated solvent sites). Dissolved solvent degradation is assumed to follow a sequential first order decay process. BIOCHLOR includes three different model types:

1. *Solute transport without decay,*
2. *Solute transport with biotransformation modeled as a sequential first-order decay process,*
3. *Solute transport with biotransformation modeled as a sequential first-order decay process with 2 different reaction zones (i.e., each zone has a different set of rate coefficient values).*

Groundwater Services, Inc., Houston, Texas, developed BIOCHLOR for the Air Force Center for Environmental Excellence (AFCEE) Technology Transfer Division at Brooks Air Force Base. The mathematical technique to solve the coupled reactive transport equations was developed by researchers formerly with the Battelle Pacific Northwest National Laboratory.

New Features in Version 2.2

BIOCHLOR Version 2.2 includes the following new features: rate constant decision support, source decay, and animation. A rate constant decision support feature was incorporated to help users estimate rate constants required for model calibration. In addition to simulating a source of constant concentration, BIOCHLOR Version 2.2 models a decaying source, which allows the simulation of both plume expansion and contraction. Lastly, an animation feature has been incorporated, which permits the visualization of plume behavior. This document describes these new features. Users should continue to refer to the existing BIOCHLOR Version 1.0 User's Manual (Aziz et al., 2000a) as the primary source of information about BIOCHLOR.

Rate Constant Decision Support For Estimating Rate Constants

A new feature in BIOCHLOR Version 2.2 is rate constant decision support, which helps users estimate rate constants to be used in BIOCHLOR simulations.

The use of an appropriate biotransformation rate constant is important, because the model is typically sensitive to the magnitude of the rate constants. Although rate constants can be taken from the literature, the values reported for a given chlorinated constituent can vary by as much as 3-4 orders of magnitude. Biotransformation rate constants are site-specific and will be dependent on the size of the dechlorinating microbial population, the availability of electron donors, and environmental conditions. Many rate constants in the general literature are derived from laboratory microcosm studies. Typically, these laboratory-derived values overestimate the rate of biotransformation seen in the field, because of the difficulty in simulating field conditions in a laboratory environment (Aziz et al., 2000b).

The best approach for determining rate constants is to calibrate BIOCHLOR to field data for a given sampling event. To estimate rate constants, change the rate constant for PCE degradation

until the PCE predicted concentrations match the PCE field data. Then, change the TCE rate constant until the TCE predicted concentrations match the field data. Continue estimating rate constants for the other constituents. In this way, site-specific rate constants are estimated, and the model is then considered calibrated. Using the site-specific rate constants, predictive simulations can be conducted by increasing the simulation time to estimate future plume behavior.

To speed the calibration process, BIOCHLOR Version 2.2 incorporates the Buschek and Alcantar (1995) rate constant estimation method, which *automatically* provides an approximate calibration of the model to entered site-specific field data. This feature can be accessed from the Biotransformation section on the input screen, by pressing the “λ Help” button. The Buschek and Alcantar approach uses the equations in Table 1, which assume 1-D dispersion, steady-state conditions, and biotransformation only in the aqueous phase. Although this equation has the potential to overestimate biotransformation rate constants by lumping the effects of lateral and vertical dispersion with biotransformation, it quickly yields a reasonable first approximation of the rate constants. These rate constant estimates can be manually refined subsequently. A minimum of four data points is required for rate constant determination. This approach is most appropriate for parent constituents. Caution should be exercised in using this approach with daughter constituents, as daughter product generation is not accounted for in this method.

The Buschek and Alcantar (1995) method starts with the 1-D steady-state solution to the advection-dispersion equation. By plotting, the contaminant concentration (on a logarithmic scale) versus distance downgradient (plotted on a linear scale), the slope (m) of the line is determined by linear regression. The biotransformation rate constant (λ) is determined using the slope (m) and the third equation in Table 1. In addition, BIOCHLOR also calculates the r² for the linear regression. This method is intended for 1-zone simulations only, because it uses all the field data entered in Section 7 of the model.

Table 1: Equations Used in Buschek and Alcantar (1995) Rate Constant Estimation Method

$C(x) = C_o \exp \left[\left(\frac{x}{2\alpha_x} \right) \left[1 - \left(1 + \frac{4\lambda\alpha_x}{v_s} \right)^{0.5} \right] \right]$ $m = \left(\frac{1}{2\alpha_x} \right) \left[1 - \left(1 + \frac{4\lambda\alpha_x}{v_s} \right)^{0.5} \right]$ $\lambda = \left[\frac{v_s}{4\alpha_x} \right] \left([1 - 2\alpha_x m]^2 - 1 \right)$	<p>where:</p> <p>λ is the biotrans. rate constant (1/yr)</p> <p>v_s is the seepage velocity (ft/yr)</p> <p>α_x is the longitudinal dispersivity (ft)</p> <p>m is the slope of the ln conc. vs. distance (1/ft)</p> <p>x is the distance downgradient (ft)</p> <p>C_o is the initial concentration (mg/L)</p> <p>C(x) is the concentration at distance x (mg/L)</p>
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Use of Literature Values

Although it is preferable to use site-specific field data to estimate rate constants, field data are not always available. In these cases, the user may opt to assume that no biotransformation is occurring (the most conservative option). Alternately, if there is evidence of biotransformation (by virtue of the production of daughter products), then literature values for the biotransformation rate constant may be used. As noted previously, it is difficult to select an appropriate biotransformation rate constant because these parameters are site-specific,

depending on the number and type of bacteria present, the amount of electron donor, and environmental conditions.

To provide users with more reasonable literature values, the BIOCHLOR model was calibrated with chlorinated solvent plume data from the BIOCHLOR database (Aziz et al., 2000b) to yield field-derived rate constants, as shown on Table 2. Most of the sites in the BIOCHLOR database had significant BTEX (electron donor) concentrations; so these rate constants should only be used at sites with evidence of significant electron donor.

Table 2: Rate Constants Estimated Using BIOCHLOR

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

Rate Constant Decision Support in BIOCHLOR

BIOCHLOR Version 2.2 provides guidance for the selection of field-derived biotransformation rate constants for chlorinated ethenes and chlorinated ethanes. This guidance is provided through the “λ Help” button in the Biotransformation section of the input screen.

The user is first asked whether there is evidence of reductive dechlorination at the site. If not, biotransformation rate constants of zero should be employed. If there is evidence of reductive dechlorination, BIOCHLOR queries the user as to the amount of electron donor present. If the concentration of electron donor is >0.1 mg/L or hydrogen concentrations are present at > 1 nM, then the user is presented with rate constants for the chlorinated constituents that range from the minimum value to the 75th percentile, as determined in the BIOCHLOR database study (Table 2). For constituents with limited data, the maximum value was used as the upper limit. If low levels of electron donor are present, but there is still evidence of biotransformation, then BIOCHLOR suggests using a rate constant less than the minimum value.

Source Decay

Dense non-aqueous phase liquids (DNAPLs), such as PCE and TCE, can act as continuing sources of groundwater contamination. The rate at which constituents in the DNAPL or source dissolve into the groundwater ultimately determines the concentration of dissolved contaminants in the plume and the lifetime of a dissolved plume.

In BIOCHLOR Version 1.0, the transport model incorporates a source term of constant concentration over time, as used in the original Domenico model (Domenico, 1987). In BIOCHLOR Version 2.2, the user has the option of modeling a source with constant or decaying concentration over time. Source decay is modeled as a first order process. This approach

captures all processes that can lead to depressed aqueous-phase concentrations in the source zone, including decreased dissolution rate from the DNAPL, biotransformation, or any other degradation processes.

After selecting the “Decaying” source option (accessed through the “**Source Options**” button on the input screen), enter a source decay rate constant, k_s , for all of the constituents. This value must be previously calculated by plotting temporal aqueous concentrations in a source area well on a semi-log plot and determining the slope as shown in Figure 1. Note that Excel will calculate a slope in units of 1/days. This slope must be converted to units of 1/yr as required by Biochlor 2.2. A new tool, called BIOSOURCE, is currently being developed for the AFCEE by Groundwater Services, Inc. This tool will assist the user in determining source decay constants. Be aware that the source decay constant, k_s , is different from the biotransformation constant, λ . k_s describes how the concentration in a source area well decreases as the DNAPL is depleted of the constituent of concern, whereas λ is the biotransformation rate constant for a constituent in the plume.

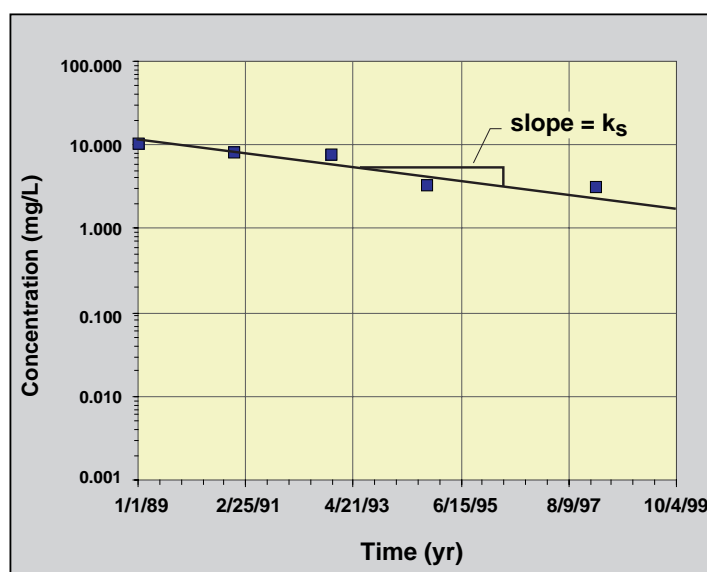


Figure 1: Determination of k_s Using Aqueous Concentrations in Source Area Wells

The equations describing groundwater transport and biotransformation with a decaying source are presented in Appendix A.1. The decaying source feature can only be used with one-zone simulations. The user is restricted to k_s values that are less than $1/R^*(\lambda+Vs/4\alpha)$ to prevent unstable complex solutions. A safety factor of 20% is also incorporated.

Animation for Centerline Output

The addition of a decaying source permits the simulation of expanding and contracting plumes as the simulation time is increased. To help the user *visualize* plume movement, an animation feature (similar to that in BIOSCREEN) is incorporated in BIOCHLOR. This animation feature can be accessed by pressing the “**Run Centerline**” button on the input screen, which directs the user to the “Individual” constituent page.

The centerline output screen shows the concentration along the centerline of the plume ($y=0$). Clicking on “**Prepare Animation**” divides the simulation into 10 separate time periods and

shows the movement of the plume based on either the Biotransformation or No Degradation model. After the first animation is completed, the user can step forward or backward in time by pressing the “Next” or “Prev” buttons, or all 10 simulations can be replayed by pressing the “Replay” button.

Revised Features

There are two minor changes to features originally present in BIOCHLOR Version 1.1. First, the longitudinal dispersivity, α_x , can now be entered directly on the input screen, or the user can press the “Calc. Alpha x” button to receive assistance with the alpha x calculation. The options for calculating alpha x remain the same as in Version 1.1; however, the relations (linear or Xu and Eckstein) are based on the estimated plume length, L_p , instead of scale, x . Whichever option is chosen, alpha x remains constant over the extent of the plume(s).

The second change involves the order of the output screens. To facilitate model calibration, the user is now directed to the “Individual” constituent page first, instead of the output page showing all the constituents simultaneously.

Troubleshooting Tips

Spreadsheet-Related Problems

The buttons won't work: BIOCHLOR 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, press the “Unprotect Sheet” button. Then, select the cell, pull down the format menu, select “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. Note that for vertical dispersivity, BIOCHLOR will convert a “0” in the data entry cell to a very low number to avoid #DIV/0! errors.

There once were formulas in some of the boxes on the input screen, but they were accidentally overwritten: Press the closest “C” button or click on the “Restore Formulas” button on the bottom right-hand side of the input screen.

The graphs seem to move around and change size: This is a feature of Excel. When graph scales are altered to accommodate different plotted data, the physical size of the graphs will change slightly, sometimes resulting in a graph that spreads out over the fixed axis legends. You can manually resize the graph to make it look nice again by double-clicking on the graph and resizing it (refer to the Excel User's Manual).

The source dialog boxes keep closing. If you press “Enter” when inputting data in a dialog box then the dialog box will close. Do not press “Enter” and move to the next cell by using the mouse

and clicking or by using tabs. If you do press “Enter” by accident, simply select your source option again.

The scale on the 3-D graphic on the array page is not even. This is a feature of Excel. There is no way of creating an even scale when using unevenly spaced data in a 3-D graphic.

Common Error Messages

Unable to Load Help File: The most common error message encountered with BIOCHLOR 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, BIOCHLR22.HLP. Here are some suggestions (in decreasing order of preference) for helping WinHelp find it:

1. If you are asked to find the requested file, do so. The file is called BIOCHLR22.HLP, and it was installed in the same directory/folder as the BIOCHLOR model file.
2. Use the File/Open menus from within Excel instead of double-clicking on the filename or Program Manager icon to open the BIOCHLOR model file. This sets the *current directory* to the directory containing the Excel file you just opened.
3. Change the WinHelp call in the VBA Module to *hard code* the directory information. That way, the file name and its full path will be explicitly passed to WinHelp. Go to the Tools menu and select Macro. Enter “btnBasic Help_click” for the macro you are searching for. This will take you to all the help files. Enter the new path.
4. As a last resort, you can add the BIOCHLOR directory to your path (located in your AUTOEXEC.BAT file), and this problem will be cured. You will have to reboot your machine, however, to make this work

Minimum System Requirements

The BIOCHLOR model requires a computer system capable of running Microsoft® Excel '97 or 2000 for Windows. Operation requires an IBM-compatible PC equipped with a Pentium II or later processor. A minimum of 64 MB of system memory (RAM) is strongly recommended.

Installation and Start-Up

The software is installed by copying the BIOCHLOR model file (BIOCHLOR22.xls) and the BIOCHLOR help file (BIOCHLR22.hlp) to the same folder on your computer hard drive. To use the software, start Excel and load the BIOCHLOR 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 BIOCHLOR to operate effectively, you must **enable** the macros.

APPENDIX A.1 DOMENICO ANALYTICAL MODEL WITH DECAYING SOURCE

To model a decaying source in BIOCHLOR, the Domenico (1987) semi-analytical solution for reactive transport with first order biological decay was modified to incorporate a decaying source (boundary) condition. The revised model assumes that the source decays exponentially via a first order expression (i.e., $C_0 \exp(-k_s t)$). The source decay constant, k_s , must be determined by the user prior to using BIOCHLOR, as discussed on page 4. The modification of the Domenico solution was accomplished by extending a 1-D solution to the advection-dispersion equation that incorporated a decaying boundary condition to a 3-D solution by analogy (Van Genuchten and Alves, 1982).

BIOCHLOR evaluates centerline concentrations at $y=0$, $z=0$ and the 2-D array at $z=0$. The boundary conditions, assumptions, limitations, and model equation are discussed below.

The initial conditions of the source decay BIOCHLOR model are:

1. $C(x, y, z, 0) = 0$ (Initial concentration = 0 for $x, y, z, > 0$)
2. $C(0, Y, Z, 0) = C_0 e^{-k_s t}$ (Source concentration for each vertical plane source = C_0 at time 0). The user can also opt to model the source as a continuous source with constant concentration as described in Appendix A.1 in the Biochlor User's Manual (Aziz et al, 2000a).

The key assumptions in the model are:

1. The aquifer and flow field are homogenous and isotropic.
2. The ground-water velocity is fast enough that molecular diffusion in the dispersion terms can be ignored (may not be appropriate for simulation of transport through clays).
3. Adsorption is a reversible process represented by a linear isotherm.

The key limitations to the model are:

1. The model should not be applied where pumping systems create a complicated flow field.
2. The model should not be applied where vertical flow gradients affect contaminant transport.
3. The model should not be applied where hydrogeologic conditions change dramatically over the simulation domain.

Modified Domenico Model with First Order Biotransformation and Source Decay	
$C(x, y, z, t) = \frac{C_o}{8} e^{-k_s t} f_x f_y f_z$	
$f_x = \exp\left(\frac{x\left[1 - (1 + 4\alpha_x(\lambda - k_s R)/v_s)^{0.5}\right]}{2\alpha_x}\right) * \operatorname{erfc}\left(\frac{x - vt(1 + 4\alpha_x(\lambda - k_s R)/v_s)^{0.5}}{2(\alpha_x vt)^{0.5}}\right) +$ $\exp\left(\frac{x\left[1 + (1 + 4\alpha_x(\lambda - k_s R)/v_s)^{0.5}\right]}{2\alpha_x}\right) * \operatorname{erfc}\left(\frac{x + vt(1 + 4\alpha_x(\lambda - k_s R)/v_s)^{0.5}}{2(\alpha_x vt)^{0.5}}\right)$	
$f_y = \operatorname{erf}\left(\frac{(y + Y/2)}{2(\alpha_y x)^{0.5}}\right) - \operatorname{erf}\left(\frac{(y - Y/2)}{2(\alpha_y x)^{0.5}}\right) \quad f_z = \operatorname{erf}\left(\frac{(z + Z)}{2(\alpha_z x)^{0.5}}\right) - \operatorname{erf}\left(\frac{(z - Z)}{2(\alpha_z x)^{0.5}}\right)$	
Definitions	
	<p>$C(x, y, z, t)$ Concentration at distance x downstream of source and distance y off centerline of plume at time t (mg/L)</p> <p>C_o Concentration in Source Area at $t=0$ (mg/L)</p> <p>x Distance downgradient of source (ft)</p> <p>y Distance from plume centerline of source (ft)</p> <p>z Distance from top of saturated zone to measurement point (assumed to be 0; concentration is always given at top of saturated zone).</p> <p>α_x Longitudinal ground-water dispersivity (ft)</p> <p>α_y Transverse ground-water dispersivity (ft)</p> <p>α_z Vertical ground-water dispersivity (ft)</p> <p>n_e Effective Soil Porosity</p> <p>λ First-Order Degradation Rate Coefficient(yr^{-1})</p> <p>v_s Seepage Velocity (ft/yr)=$Ki/(n_e)$</p> <p>v Chemical Velocity (ft/yr)=v_s/R</p> <p>K Hydraulic Conductivity (ft/yr)</p> <p>R Constituent retardation factor</p> <p>i Hydraulic Gradient (cm/cm)</p> <p>Y Source Width (ft)</p> <p>Z Source Thickness (ft)</p> <p>k_s Source Decay Constant ($1/\text{yr}$)</p>

The most important modifications to the original Domenico model are:

1. An exponentially decaying source boundary condition is employed instead of a constant source.
2. Biotransformation is assumed to occur only in the aqueous phase. The original Domenico model was derived assuming that biotransformation occurred equally rapidly in the soil and aqueous phases. To make this adjustment, the rate constants were divided by the retardation factor.
3. To simulate a spatially-varying source, BIOCHLOR superimposes three Domenico models, each with a different concentration and source width (Connor *et al.*, 1994). The original Domenico model was derived for a single planar source of constant concentration.

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