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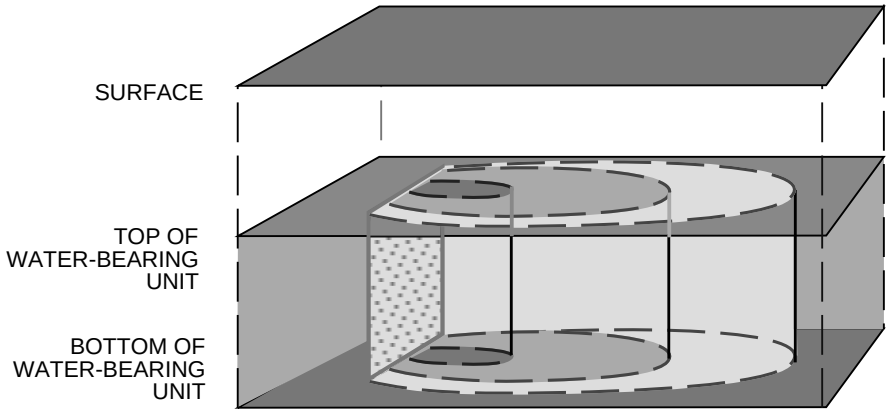
BIOCHLOR

Natural Attenuation Decision Support System

User's Manual
Version 1.0



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Natural Attenuation Decision Support System

User's Manual
Version 1.0

by

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NOTICE

The information in this document was developed through a collaboration between the U.S. EPA (Subsurface Protection and Remediation Division, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center, Ada, Oklahoma [RSKERC]) and the U.S. Air Force (U.S. Air Force Center for Environmental Excellence, Brooks Air Force Base, Texas). EPA staff contributed conceptual guidance in the development of the BIOCHLOR mathematical model. To illustrate the appropriate application of BIOCHLOR, EPA contributed field data generated by EPA staff supported by ManTech Environmental Research Services Corp, the in-house analytical support contractor at the RSKERC. The computer code for BIOCHLOR was developed by Groundwater Services, Inc. through a contract with the U.S. Air Force. Groundwater Services, Inc. also provided field data to illustrate the application of the model.

All data generated by EPA staff or by ManTech Environmental Research Services Corp were collected following procedures described in the field sampling Quality Assurance Plan for an in-house research project on natural attenuation, and the analytical Quality Assurance Plan for ManTech Environmental Research Services Corp. The development of BIOCHLOR and its User's Manual were not funded by the U.S. EPA and as such are not subject to the Agency's QA requirements.

An extensive investment in site characterization and mathematical modeling is often necessary to establish the contribution of natural attenuation at a particular site. BIOCHLOR is offered as a screening tool to determine whether it is appropriate to invest in a full-scale evaluation of natural attenuation at a particular site. Because BIOCHLOR incorporates a number of simplifying assumptions, it is not a substitute for the detailed mathematical models that are necessary for making final regulatory decisions at complex sites.

BIOCHLOR and its User's Manual have undergone external and internal peer review conducted by the U.S. EPA and the U.S. Air Force. However, BIOCHLOR is made available on an *as-is* basis without guarantee or warranty of any kind, express or implied. Neither the United States Government (U.S. EPA or U.S. Air Force), Ground Water Services, Inc., any of the authors nor reviewers accept any liability resulting from the use of BIOCHLOR or its documentation. Implementation of BIOCHLOR and interpretation of the predictions of the model are the sole responsibility of the user.

FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet these mandates, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory is the Agency's center for investigation of technological and management approaches for reducing risks from threats to human health and the environment. The focus of the Laboratory's research program is on methods for the prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites and ground water; and prevention and control of indoor air pollution. The goal of this research effort is to catalyze development and implementation of innovative, cost-effective environmental technologies; develop scientific and engineering information needed by EPA to support regulatory and policy decisions; and provide technical support and information transfer to ensure effective implementation of environmental regulations and strategies.

This screening tool will allow ground water remediation managers to identify sites where natural attenuation is most likely to be protective of human health and the environment. It will also allow regulators to carry out an independent assessment of treatability studies and remedial investigations that propose the use of natural attenuation.

Clinton W. Hall, Director
Subsurface Protection and Remediation Division
National Risk Management Research Laboratory

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BIOCHLOR was developed by Drs. Carol Aziz and Charles Newell (Groundwater Services, Inc., Houston, TX). Customization and testing of the BIOCHLOR solution engine was performed by Drs. Prabhakar Clement and Yunwei Sun (Battelle Pacific Northwest National Laboratory, Richland, WA).

The authors would like to acknowledge the U.S. Air Force Center for Environmental Excellence (AFCEE) for supporting the development of BIOCHLOR. We would like to specifically acknowledge Marty Faile and Jim Gonzales.

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The BIOCHLOR software and manual was reviewed by a distinguished review team. We wish to acknowledge members of the team for their comments and suggestions:

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Introduction

BIOCHLOR is an easy-to-use screening model that simulates remediation by natural attenuation (RNA) of dissolved solvents at chlorinated solvent release sites. 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). Reductive dechlorination is assumed to occur under anaerobic conditions and 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 two different reaction zones (i.e., each zone has a different set of rate coefficient values).*

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

Intended Uses for BIOCHLOR

BIOCHLOR attempts to answer the following fundamental question regarding RNA:

- **How far will a dissolved chlorinated solvent plume extend if no engineered controls or source area reduction measures are implemented?**

  BIOCHLOR uses an analytical solute transport model with sequential first-order decay for simulating in-situ biotransformation (Sun et al., 1999a; Sun and Clement, 1999). The model will predict the maximum extent of dissolved-phase plume migration, which may then be compared to the distance to potential points of exposure (e.g., drinking water wells, ground-water discharge areas, or property boundaries). Analytical ground-water transport models have seen wide application for this purpose (e.g., ASTM, 1995) and experience has shown such models can produce reliable results when site conditions in the plume area are relatively uniform.

BIOCHLOR is intended to be used in two ways:

1. **As a screening-level model to determine if RNA is feasible at a chlorinated solvent site.**

   BIOCHLOR is intended to be used as a *screening-level* model to determine if natural attenuation is occurring at sufficient rates at a site to warrant a full natural attenuation study. Ideally, site-specific biotransformation rate constants should be employed, but literature values can be used if measured rate constants are unavailable. Other useful attributes of BIOCHLOR include the facilitation of site characterization data organization and the ability to carry out many simulations in short periods of time. For fuel hydrocarbon release sites, the BIOSCREEN model (Newell et al., 1996) is more appropriate.

2. **As an RNA ground-water model to address selected chlorinated solvent problems**

   The Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water (U.S. EPA, 1998) describes how ground-water models, in conjunction with other types of analysis, can be used to evaluate the effectiveness of natural attenuation. BIOCHLOR is an appropriate model at sites where simplifying assumptions (e.g., uniform ground-water flow, a vertical plane source, first-order decay) can be

made so that the resulting simulations provide useful information for the problem being addressed. At other sites, where these assumptions do not hold, a more sophisticated numerical model such as RT3D (Clement, 1997) would be appropriate. As with any modeling study, the authors recommend that proper care be used to select the model that is best suited to 1) the source, hydrogeology, and biotransformation processes present at the site and, 2) the type of problem being addressed (e.g., screening of alternatives, providing supporting evidence of natural attenuation, developing detailed design information).

BIOCHLOR has the following limitations:

1. As an analytical model, BIOCHLOR assumes simple ground-water flow conditions.

   The model should not be applied where pumping systems create a complicated flow field. In addition, the model should not be applied where vertical flow gradients affect contaminant transport. (Note that a vertical distribution of chlorinated solvents throughout the saturated zone does not preclude the use of BIOCHLOR, as this phenomenon is related to the initial vertical migration of dense non-aqueous phase liquids in source areas.)

2. As a screening tool, BIOCHLOR assumes uniform hydrogeologic and environmental conditions over the entire model area.

   Being an analytical model, BIOCHLOR assumes constant source, hydrogeological, and biological property values for the entire model area and, therefore, simplifies actual site conditions. For this reason, the model should not be applied where extremely detailed, accurate results that closely match site conditions are required. More comprehensive numerical models should be applied in such cases.

3. BIOCHLOR is primarily designed for simulating the sequential reductive dechlorination of chlorinated ethanes and ethenes.

   The sequential biotransformation feature in BIOCHLOR should not be used for compounds that do not degrade via sequential first-order kinetics. While the interface is designed for simulating the biotransformation of chlorinated ethenes (i.e., PCE, TCE, DCE, and vinyl chloride (VC)) and chlorinated ethanes (i.e., TCA, DCA, and chloroethane (CA)), the model can be adapted for other sequential decay reactions by experienced users (see Appendix A.2).

Fundamentals of Natural Attenuation

Overview of Natural Attenuation

"Natural Attenuation" refers to naturally-occurring processes in soil and ground-water environments that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in those media. These in-situ processes include biotransformation, dispersion, dilution, adsorption, volatilization, and chemical or biological stabilization or destruction of contaminants (U.S.EPA, 1998).

Biotransformation can often be a dominant process in the natural attenuation of chlorinated solvents. At chlorinated solvent contaminated sites, most of the solvent degradation occurs by reductive dechlorination (U.S.EPA, 1998). Reductive dechlorination is a microbially-mediated reaction whereby a chlorine atom on the chlorinated solvent is replaced by a hydrogen atom (Vogel and McCarty, 1987). In many bioremediation processes, an organic contaminant (such as benzene) acts as an electron donor and another substance (such as oxygen, nitrate, etc.) acts as the electron acceptor. However, during reductive dechlorination, hydrogen acts as the *electron donor* and halogenated compounds, such as chlorinated solvents, act as *electron acceptors* and thus become reduced, as shown in the following half reaction:

$$R\text{-}Cl + H^+ + 2e^- \longrightarrow R\text{-}H + Cl^-$$

Figure 1 shows the reductive transformation pathways for the common chlorinated aliphatics. More details on the biotransformation of chlorinated solvents can be found in Appendix A.2.

Reductive dechlorination can be modeled as a sequential first-order decay process. This means that a parent compound undergoes first-order decay to produce a daughter product and that product undergoes first-order decay and so on. Generally, the more highly chlorinated the compound, the more rapidly it is reduced by reductive dechlorination (Vogel and McCarty, 1985; Vogel and McCarty, 1987). Therefore, it is possible for daughter products to increase in concentration before they decrease as shown in Figure 2. BIOCHLOR accounts for sequential first-order decay of this nature, and this sets it apart from BIOSCREEN (Newell et al., 1996), which models the biodegradation of fuel hydrocarbons via first-order decay or electron acceptor-limited (instantaneous reaction) processes.

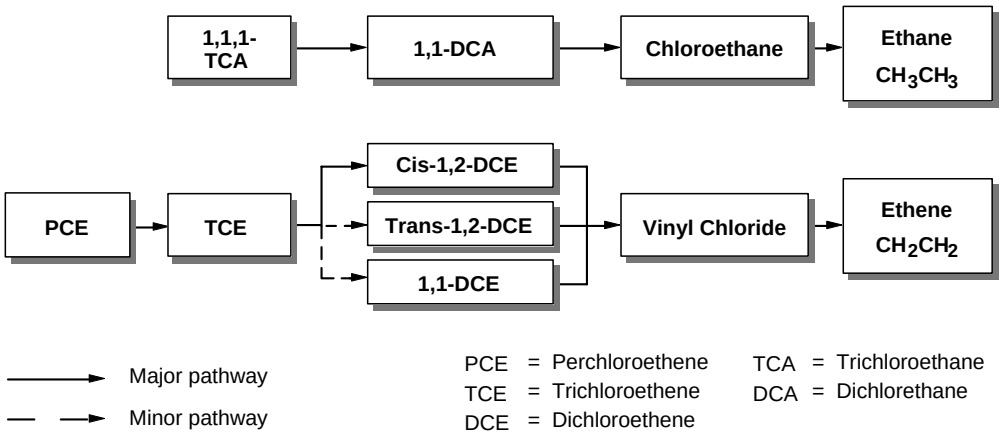


Figure 1. Reductive dechlorination pathways for common chlorinated aliphatic hydrocarbons (after Vogel and McCarty,1985; Vogel and McCarty,1987).

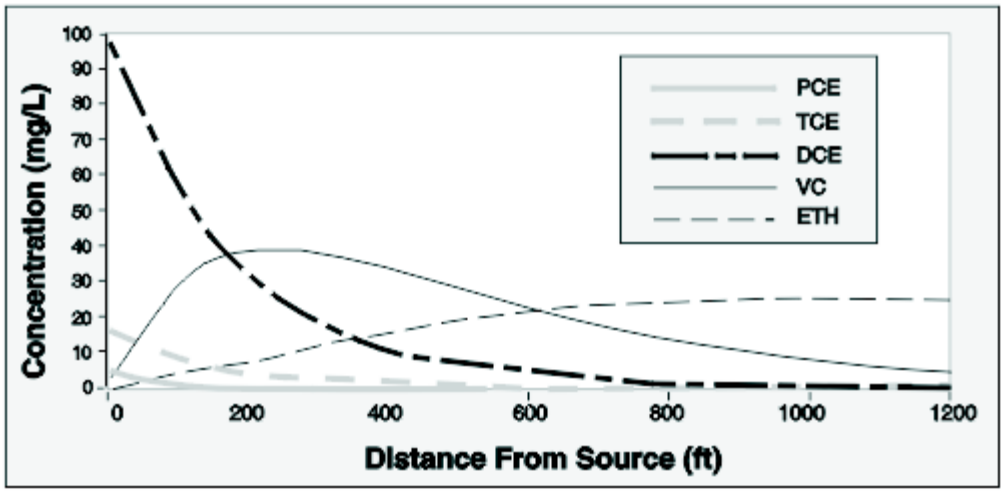


Figure 2. Reductive transformation of chlorinated ethenes.

For biological reductive dechlorination to occur, the following conditions must exist:

1. The subsurface environment must be anaerobic and have a low oxidation-reduction potential (ORP).
2. Chlorinated solvents that are amenable to reductive dechlorination must be present.
3. A population of dechlorinating bacteria must be present.
4. An adequate supply of fermentation substrates to produce dissolved hydrogen must be present.

The environmental chemistry and the ORP of a site play an important role in determining whether reductive dechlorination will occur. Based on thermodynamic considerations, reductive dechlorination will occur only after both oxygen and nitrate have been depleted from the aquifer, because oxygen and nitrate are more energetically favorable electron acceptors than chlorinated solvents when hydrogen is the electron donor (U.S. EPA, 1998).

The role of hydrogen as an electron donor during reductive dechlorination is now widely recognized as a key factor governing the dechlorination of chlorinated compounds (Gossett and Zinder, 1996; Holliger et al., 1993; Maymo-Gatell et al., 1997; Hughes et al., 1997; Carr and Hughes, 1998). The hydrogen is produced in the terrestrial subsurface by the fermentation of a wide variety of organic compounds including anthropogenic compounds such as petroleum hydrocarbons and natural organic matter. Hydrogen is then used by the dechlorinating bacteria as an electron donor.

Although BIOCHLOR primarily models the degradation of chlorinated solvents via reductive dechlorination, which occurs under highly reduced anaerobic conditions, some of the chlorinated solvents may degrade under aerobic conditions. TCE, c-DCE and VC degrade cometabolically (McCarty and Semprini, 1994) and VC (Hartmans et al., 1985; Hartmans and de Bont, 1992) and possibly c-DCE (Bradley and Chapelle, 1998) can be directly oxidized to carbon dioxide under aerobic conditions. PCE has not been found to degrade aerobically (McCarty and Semprini, 1994).

Natural Attenuation Lines of Evidence and the Role of BIOCHLOR

To support remediation by natural attenuation, it must be scientifically demonstrated that attenuation of the site contaminants is occurring at rates sufficient to be protective of human health and the environment. According to the "Technical Protocol For Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water" (U.S. EPA, 1998), three lines of evidence can be used to support natural attenuation of chlorinated solvents including :

1. Observed reductions in contaminant **concentrations** along the flow path downgradient from the source of contamination.
2. Documented loss of contaminant **mass** at the field scale using:
   a) Chemical and geochemical analytical data including decreasing parent compound concentration, increasing daughter compound concentrations, depletion of electron acceptors and donors, and increasing metabolic byproduct concentrations; and/or
   b) A rigorous estimate of residence time along the flow path to document contaminant mass reduction and to calculate biological decay rates at the field scale.
3. Laboratory microcosm or field data that support the occurrence of biotransformation and give rates of biotransformation.

At a minimum, the investigator must obtain the first two lines of evidence or the first and third lines of evidence. The second or third line of evidence is crucial because it provides biotransformation rate constants. These rate constants can be used in conjunction with other fate and transport parameters to predict contaminant concentration and to assess risk at a downgradient point of exposure (U.S. EPA, 1998).

Compared to fuel hydrocarbon plumes, use of natural attenuation as a stand-alone remedy for chlorinated solvent plumes is appropriate for a much lower percentage of plumes, because of their longer plume lengths. Therefore, it is particularly important to make an accurate assessment of the potential for natural attenuation prior to investing in a detailed natural attenuation study. To assist in this endeavor, the natural attenuation screening process is outlined in Figure 3. The shaded steps indicate the stages where BIOCHLOR plays a role in the screening process.

The first shaded stage (i.e., "Is Biodegradation Occurring?") is the stage where the natural attenuation scoring system comes into play. The scoring system requires the concentrations of electron acceptors, parent and daughter chlorinated solvents, methane, TOC, and chloride and ORP, temperature, and pH measurements (U.S. EPA, 1998). These field data are evaluated and scored for evidence of biotransformation. BIOCHLOR incorporates this scoring system, which can be accessed from the input page.

If there is evidence of biotransformation, BIOCHLOR may be used subsequently to compare the rate of chlorinated solvent transport without biotransformation to the rate of attenuation with biotransformation. Being a transient model, the simulation time can be varied to determine the future extent of contamination. Field-derived biological rate coefficients should be used if possible, but literature values may be used in the absence of site-specific rate constants or the model may be calibrated to field data.

The primary purpose of comparing the transport rate to the attenuation rate is to determine if the residence time along the flow path is adequate to protect human health and the environment (i.e., to estimate if the contaminant degrades to an acceptable concentration before receptors are exposed). In the case of rate coefficients or any other parameter that is not known accurately or that varies over the extent of the plume, sensitivity analyses should be conducted. If modeling shows that the receptors will not be impacted by contaminants at concentrations above regulatory criteria, then the screening criteria are met, and the investigator can proceed with a full natural attenuation evaluation. Details of a full natural attenuation evaluation can be found in "Technical Protocol For Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water" (U.S. EPA, 1998).

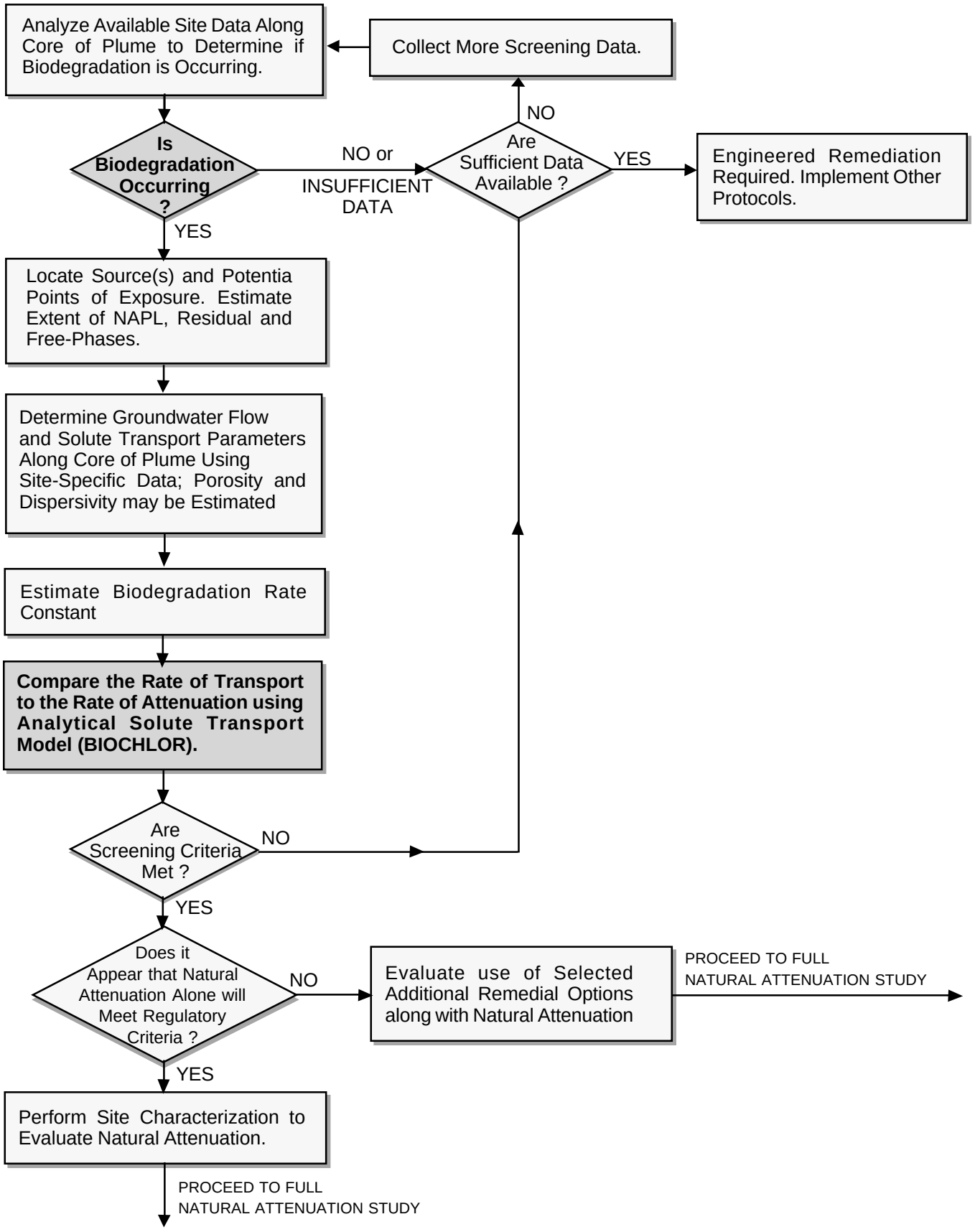


Figure 3. Initial screening process flow chart.

BIOCHLOR Concepts

The BIOCHLOR Natural Attenuation software is based on a sequential, first-order, coupled reactive transport model. The transport problem is analytically solved using the Domenico model (1987) by uncoupling the transport equations using a novel analytical strategy (Sun *et al*., 1999a, 1999b; Sun and Clement, 1999) as discussed in Appendix A.3. The original Domenico model assumes a fully-penetrating vertical plane source oriented perpendicular to ground-water flow to simulate the release of organics to moving ground water and accounts for the effects of one-dimensional advective transport, three-dimensional dispersion, linear adsorption, and first-order decay. In BIOCHLOR, the Domenico solution has been adapted to provide three different model types representing i) transport with no decay, ii) transport with sequential first-order decay in one zone, and iii) transport with sequential first-order decay in two zones (see Model Types). Guidelines for selecting key input parameters for the model are outlined in BIOCHLOR Input Parameters. For help on Output, see BIOCHLOR Output.

BIOCHLOR Model Types

The software allows the user to view results from three different types of ground-water transport models:

1. **Solute transport with no decay.** This model is appropriate for predicting the movement of conservative (non-degrading) solutes. The only attenuation mechanisms are dispersion in the longitudinal, transverse, and vertical directions (if present), and adsorption of contaminants to the soil matrix (if present).

2. **Solute transport with sequential first-order decay in one zone.** With this model, the reactive transport of both parent and daughter chlorinated solvents can be modeled. This model accounts for dispersion, adsorption, advection, and sequential biotransformation. The reductive dechlorination of the parent solvent to daughter product is assumed to be a first-order process. That is, the solute degradation rate is assumed to be proportional to the solute concentration. However, the daughter products are also *produced* by the first-order degradation of the preceding parent compound. Therefore, the daughter product can simultaneously undergo both production and degradation. "One zone" means that one set of rate constants is used within the model area. The model assumes that biotransformation starts immediately downgradient of the source and that no biotransformation of dissolved constituents in the source area occurs.

   The sequential first-order decay model does not directly account for site-specific information such as the concentration of the electron donor (i.e., hydrogen) or the number of dechlorinating bacteria; this is implicitly accounted for in the first-order decay rate coefficient supplied by the user. Ideally, rate coefficients measured in the field or derived from model calibration to site data should be used. Literature values may also be employed, but the user must be aware that the literature value may have been measured under different environmental conditions than those present for the plume being modeled.

3. **Solute transport with sequential first-order decay in two zones.** This model employs the same sequential first-order decay kinetics as the preceding model but allows the user to use two different sets of rate constants within the model area. This may be appropriate for plumes that undergo rapid biotransformation close to the source where there is an excess of fermentable substrates but negligible biotransformation further downgradient where fermentable substrates have been depleted or for plumes that go from anaerobic conditions to aerobic conditions. Aerobic conditions can be considered only in the second zone and should be modeled only by experienced users as discussed in Appendix A.2.

   Note: This two-zone model should be employed only when the plume is at steady-state throughout the first zone. The plume is at steady-state if plume concentrations (field measurements or model predictions) are not changing with time. This condition is required to ensure the constant concentration boundary condition at the boundary between zone 1 and zone 2. Refer to Appendix A.2 for a more detailed discussion.

BIOCHLOR Data Entry

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 Data Set" button on the lower right portion of the input screen.
2. Because BIOCHLOR 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.

3. Parameters used in the model can be entered directly into the white cells or they can be calculated by the model using data entered in the gray cells (e.g., seepage velocity can be entered directly or calculated using hydraulic conductivity, gradient, and effective porosity), followed by pressing the "C" button.

NOTE: Although literature values are provided, it is strongly recommended that the user employ measured hydrogeological and biotransformation values whenever possible. 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. Examples of a sensitivity analysis can be found in Appendix A.7.

1. Hydrogeologic Data

Parameter	***Seepage Velocity (Vs)***
Units	ft/yr
Description	Actual interstitial ground-water velocity, equaling Darcy velocity divided by effective porosity. Note that the Domenico model and BIOCHLOR are not formulated to simulate the effects of chemical diffusion. Therefore, contaminant transport through very slow hydrogeologic regimes (e.g., clays and slurry walls) should probably not be modeled using BIOCHLOR unless the effects of chemical diffusion are proven to be insignificant.
Typical Values	0.5 to 200 ft/yr
Source of Data	Calculated by multiplying hydraulic conductivity by hydraulic gradient and dividing by effective porosity. It is strongly recommended that actual site data be used for hydraulic conductivity and hydraulic gradient data parameters; effective porosity can be estimated.
How to Enter Data	1) Enter directly or 2) Fill in values for hydraulic conductivity, hydraulic gradient, and effective porosity as described below and have BIOCHLOR calculate seepage velocity by pressing the "C" button.

Parameter	***Hydraulic Conductivity (K)***
Units	cm/sec
Description	Horizontal hydraulic conductivity of the saturated porous medium.
Typical Values	Clays: $<1x10^{-6}$ cm/s Silts: $1x10^{-6}$ - $1x10^{-3}$ cm/s Silty sands: $1x10^{-5}$ - $1x10^{-1}$ cm/s Clean sands: $1x10^{-3}$ - 1 cm/s Gravels: > 1 cm/s
Source of Data	Pump tests or slug tests at the site. It is strongly recommended that actual site data be used for all RNA studies.
How to Enter Data	Enter directly. If seepage velocity is entered directly, this parameter is not needed in BIOCHLOR.

Parameter	***Hydraulic Gradient (i)***
Units	ft/ft
Description	The slope of the potentiometric surface. In unconfined aquifers, this is equivalent to the slope of the water table.
Typical Values	0.0001 - 0.05 ft/ft
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. If seepage velocity is entered directly, this parameter is not needed in BIOCHLOR.

1. Hydrogeologic Data, cont.

Parameter	***Effective Porosity (n)***
Units	unitless
Description	Dimensionless ratio of the volume of interconnected voids to the bulk volume of the aquifer matrix. Note that "total porosity" is the ratio of all voids (included 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% (Smith and Wheatcraft, 1993).
Typical Values	Values for Effective Porosity: Clay 0.01 - 0.20; Silt 0.01 - 0.30; Fine Sand 0.10 - 0.30; Medium Sand 0.15 - 0.30; Coarse Sand 0.20 - 0.35; Gravel 0.10 - 0.35 Sandstone 0.005 - 0.10; Unfract. Limestone 0.001 - 0.05; Fract. Granite 0.00005 - 0.01 *(From Wiedemeier et al., 1995; originally from Domenico and Schwartz, 1990 and Walton, 1988).*
Source of Data	Typically estimated. One commonly used value for silts and sands is an effective porosity of 0.25. The ASTM RBCA Standard (ASTM, 1995) includes a default value of 0.38 (to be used primarily for unconsolidated deposits).
How to Enter Data	Enter directly. Note that if seepage velocity is entered directly, this parameter is still needed to calculate the retardation factor and plume mass flux.

2. Dispersivity

Parameter	***Longitudinal Dispersivity (alpha x)*** ***Transverse Dispersivity (alpha y)*** ***Vertical Dispersivity (alpha z)***
Units	ft
Description	Dispersion refers to the process whereby a dissolved solvent will be spatially distributed longitudinally (along the direction of ground-water flow), transversely (perpendicular to ground-water flow), and vertically (downward) 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. Selection of dispersivity values is a difficult process, given the impracticability of measuring dispersion in the field. 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. Researchers indicate that dispersivity values can range over 2-3 orders of magnitude for a given value of plume length or distance to measurement point (Gelhar *et al*., 1992). For more information on dispersivity, see Appendix A.4.
Typical Values	The user also has the option to enter a fixed diffusivity value or dispersivity relation as a function of x (distance from the source in ft). BIOCHLOR is programmed with some commonly used relations based on scale that are representative of typical and low-end dispersivities. A fixed dispersivity value should be used for 2-zone simulations. **• Longitudinal Dispersivity** The user is given three options: ***Option 1*** (the default option) allows the user to specify a fixed value for alpha x. One commonly used relation is to assume that alpha x is 10% of the estimated plume length. This option is required for conducting 2-zone biotransformation simulations. ***Option 2*** assumes that alpha x = 0.1* x *(Pickens and Grisak, 1981)* ***Option 3*** calculates the longitudinal dispersivity using the following correlation: Alpha x = $3.28 \cdot 0.28 \cdot \left[\log_{10}\left(\frac{x}{3.28}\right)\right]^{2.446}$ *(Xu and Eckstein, 1995; Al-Suwaiyan, 1996)* **• Transverse Dispersivity** The user may choose a ratio of alpha y : alpha x. One commonly used ratio is: Alpha y: alpha x = 0.10 *(Based on high reliability points from Gelhar et al., 1992)* **• Vertical Dispersivity** The user may choose a ratio of alpha z : alpha x. One commonly used ratio is: Alpha z: alpha x = 0.05 *(ASTM, 1995)* Alternatively, alpha z :alpha x can be set to a very low number (e.g., E-99) to yield a conservative estimate of vertical dispersion. This is the default value used in BIOCHLOR. Other commonly used relations include: Alpha x = 0.1 Lp *(Pickens and Grisak, 1981)* Alpha y = 0.33 alpha x *(ASTM, 1995) (EPA, 1986)* Alpha z = 0.025 alpha x to 0.1 alpha x *(EPA, 1986)*
Source of Data	Typically estimated using the relations provided above (see Appendix A.4).
How to Enter Data	Click on "Change Alpha x Calc. Method" button. Select an option for alpha x. If you select Option 1, enter a fixed value in the box. Enter ratios for alpha y and alpha z. (Note: If the "Reset" button is depressed, then the following are the default options and values used by BIOCHLOR: Option 1 (fixed value) is used to calculate alpha x. The user must input a value. The alpha y : alpha x ratio is set to 0.1 and the alpha z : alpha x ratio is set to 1×10^{-99}.)

3. Adsorption Data

Parameter	*Retardation Factor (R)*
Units	unitless
Description	Adsorption to the soil matrix can reduce the concentration of dissolved contaminants moving through the ground water. The retardation factor is the ratio of the ground-water seepage velocity to the rate that organic chemicals migrate in the ground water. A retardation value of 2 indicates that if the ground-water seepage velocity is 100 ft/yr, then the organic chemicals migrate at approximately 50 ft/yr. The degree of retardation depends on both aquifer and constituent properties.
Typical Values	1 to 6 (for solvents in typical shallow aquifers)
Source of Data	Usually estimated from soil and chemical data using variables described below (ρ_b = bulk density, n = effective porosity, K_{oc} = organic carbon-water partition coefficient, K_d = distribution coefficient, and f_{oc} = fraction organic carbon on uncontaminated soil) with the following expression: $R = 1 + \frac{K_d \rho_b}{n}$ where $K_d = K_{oc} \cdot f_{oc}$ When biotransformation rates are insignificant, the retardation factor can be estimated by comparing the plume length of an adsorbed compound to the plume length of a conservative (non-adsorbing) compound.
How to Enter Data	1)Enter the retardation factor for each constituent directly. Do **NOT** press the "C" button. The worksheet will be updated automatically. OR 2) Fill in the estimated values for bulk density, partition coefficient, effective porosity, and fraction organic carbon and calculate the retardation factor by pressing the "C" button. **Common R**: BIOCHLOR uses one retardation factor for all the constituents, not individual retardation factors. Currently, BIOCHLOR calculates the median retardation factor and uses that value in all calculations. Alternatively, the user can enter another retardation value in the cell beside Common R. The Common R value that is chosen should be representative of the retardation factors of the constituents modeled. In addition, sensitivity analyses should be conducted to evaluate the effect of the choice of the common retardation factor on the results (see Appendix A.7 for an example).

Parameter	*Aquifer Matrix Bulk Density (ρ_b)*
Units	kg/L or g/cm^3
Description	Bulk density, in kg/L, of the aquifer matrix (related to porosity and pure solids density).
Typical Values	Although this value can be measured in the lab, in most cases estimated values are used. A value of 1.7 kg/L 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 kg/L.
How to Enter Data	Enter directly. If the retardation factor is entered directly, this parameter is not needed in BIOCHLOR.

3. Adsorption Data, cont.

Parameter	***Organic Carbon Partition Coefficient (K_{oc})***
Units	(mg/kg) / (mg/L) or (L/kg) or (mL/g)
Description	Chemical-specific partition coefficient between soil organic carbon and the aqueous phase. Larger values indicate greater affinity of contaminants for the organic carbon fraction of soil.
Typical Values	Perchloroethylene 426 L/kg Trichloroethylene 130 L/kg Dichloroethylene 125 L/kg Vinyl Chloride 29.6 L/kg (at 20 °C) *(Note that there is a wide range of reported values and these values are temperature-dependent)*
Source of Data	Chemical reference literature or relations between K and solubility or K and the octanol-water partition coefficient (K_{ow}).
How to Enter Data	Enter directly. If the retardation factor is entered directly, this parameter is not needed in BIOCHLOR.

Parameter	***Fraction Organic Carbon (f_{oc})***
Units	unitless
Description	Fraction of the aquifer soil matrix comprised of natural organic carbon in uncontaminated areas. More natural organic carbon means more adsorption of organic constituents on the aquifer matrix.
Typical Values	0.0002 - 0.02
Source of Data	The fraction organic carbon value should be measured, if possible, by collecting a sample of aquifer material from an uncontaminated area and performing a laboratory analysis (e.g., ASTM Method 2974-87 or equivalent). If unknown, a default value of 0.001 is often used (LaGrega et al., 1994).
How to Enter Data	Enter directly. If the retardation factor is entered directly, this parameter is not needed in BIOCHLOR.

4. Biotransformation Data

Parameter	***First-Order Decay Coefficients (lambda) for Zones 1 and 2***
Units	1/yr
Description	Rate coefficient describing first-order decay process for dissolved constituents. The first-order decay coefficient equals 0.693 divided by the half-life of the contaminant in ground water. If a dissolved solvent is undergoing first order decay only, the rate of biotransformation depends on the concentration of the contaminant and the rate coefficient. In the case of sequential first order decay, the solvent is assumed to degrade by first order kinetics, but it is also simultaneously being produced by the first order decay of the preceding compound (see Appendix A.2). Considerable care must be exercised in the selection of a first-order decay coefficient for each constituent to avoid significantly over-predicting or under-predicting actual decay rates. For guidance on how to model your site assuming one or two biotransformation zones, see General Data, Section 5.
Typical Values	Perchloroethylene 0.07 to 1.20 yr^{-1} Trichloroethylene 0.05 to 0.9 yr^{-1} cis-1,2-Dichloroethylene 0.18 to 3.3 yr^{-1} Vinyl Chloride 0.12 to 2.6 yr^{-1} *(from Wiedemeier et al., 1999)* Note: The equations in BIOCHLOR cannot accept a zero value for any of the rate coefficients. BIOCHLOR checks entered values and assigns a low value if zero is entered. Also, no two rate constants in the same zone can be identical. BIOCHLOR will issue an error message and ask the user to re-enter the rate coefficients.
Source of Data	Optional methods for selection of appropriate decay coefficients are as follows: **Calibrate to Existing Plume Data:** BIOCHLOR can be used to determine first-order decay coefficients that best match the observed site concentrations. One may adopt a trial-and-error procedure to derive a best-fit decay coefficient for each contaminant by varying the decay coefficient until predicted concentrations match measured concentrations. **Literature Values:** Various published references are available listing biotransformation rate coefficients (e.g., USEPA, 1998; Howard et al., 1991). Many references report the half-lives; these values can be converted to the first-order decay coefficients using $k = 0.693 / t$ (see dissolved solvent half-life). **Note:** Because the use of literature values may overestimate the amount of biotransformation occurring, the user should conduct sensitivity analyses to determine the impact of the chosen rate coefficients on plume lengths (see Appendix A.7). **Other Methods:** The "Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water" (USEPA, 1998) describes other methods for obtaining rate coefficients, including the use of microcosm data and use of field-scale tracer data.
How to Enter Data	1) Enter directly or 2) Fill in the estimated half-life values as described below and have BIOCHLOR calculate the first-order decay coefficients by pressing the "C" button.

4. Biotransformation Data, cont.

Parameter	***Dissolved Solvent Half-Life ($t_{1/2}$)***
Units	years
Description	Time, in years, for dissolved plume concentrations to decay by one half as contaminants migrate through the aquifer. The amount of degradation that occurs is related to the time the contaminants spend in the aquifer. Considerable care must be exercised in the selection of a half-life for each contaminant in order to avoid significantly over-predicting or under-predicting actual decay rates.
Typical Values	Perchloroethylene 0.58 to 9.9 yr Trichloroethylene 0.77 to 13.9 yr cis-1,2-Dichloroethylene 0.21 to 3.9 yr Vinyl Chloride 0.27 to 5.8 yr (from Wiedemeier et al., 1999)
Source of Data	Optional methods for selection of appropriate half-lives are the same as for the rate coefficients
How to Enter Data	Enter directly in gray cells and press the "C" button. If the first-order decay coefficient is entered directly, this parameter is not needed in BIOCHLOR.

Parameter	***Abiotic First Order Rate Coefficient (1/yr)***
Units	1/years
Description	Rate coefficient describing first-order abiotic decay process for chloroethane. Chloroethane degrades to ethanol under abiotic conditions. Note: Although 1,1,1-TCA can abiotically decay to 1,1-DCE via elimination and to acetic acid as a result of hydrolysis, BIOCHLOR cannot simulate abiotic decay and chlorinated ethane daughter product generation simultaneously. BIOCHLOR can be used to simulate the degradation of 1,1,1-TCA alone by setting the initial daughter product concentrations to zero, the biological rate constants for DCA and CA to zero, and entering a TCA degradation rate coefficient on the input page. This rate coefficient represents the sum total of all abiotic and biotic coefficients for processes observed in the field at your site. BIOCHLOR will generate TCA predictions, but daughter product predictions should be ignored. Note that the abiotic rate coefficients for the chlorinated ethenes are very slow (greater than 10^6 years half-life, (Jeffers et al., 1989)) and therefore abiotic degradation can be ignored for PCE, TCE, DCE, and VC.
Typical Values	chloroethane to ethanol 0.37 yr^{-1} (20°C) 1,1,1-trichloroethane to 1,1-DCE 0.058-0.32 yr^{-1} (10-20 °C) 1,1,1-trichloroethane to acetic acid 0.25 to 0.41 yr^{-1} *(from Vogel and McCarty, 1987; McCarty, 1996)*
Source of Data	Optional methods for selection of appropriate rate coefficients are as follows: **Literature Values:** Various published references are available that list rate coefficients for hydrolysis and other abiotic processes (e.g., Howard et al., 1991).
How to Enter Data	Press "λ_A" button. Enter values in the dialog box and press "OK".

4. Biotransformation Data, cont.

Parameter	***Yield***			
Units	unitless			
Description	Because biotransformation rate expressions are calculated on a molar basis and BIOCHLOR accepts concentration data on a mass basis (i.e., mg/L), a conversion factor must be incorporated to account for the amount of mass of daughter product produced from the degradation of the parent compound. The yield is the ratio of the daughter product molecular weight to the parent compound molecular weight. Note: This is NOT the biomass yield.			
Typical Values	*TCE/PCE*	*0.795*	*DCA/TCA*	*0.742*
	DCE/TCE	*0.737*	*CA/DCA*	*0.652*
	VC/DCE	*0.645*	*ETHA/CA*	*0.465*
	ETH/VC	*0.450*		
Sources of Data	Values for the chlorinated ethenes and ethanes have been provided. The user only needs to input yields if working with other substances that decay by sequential first order decay.			
How to Enter Data	Enter directly.			

5. General Data

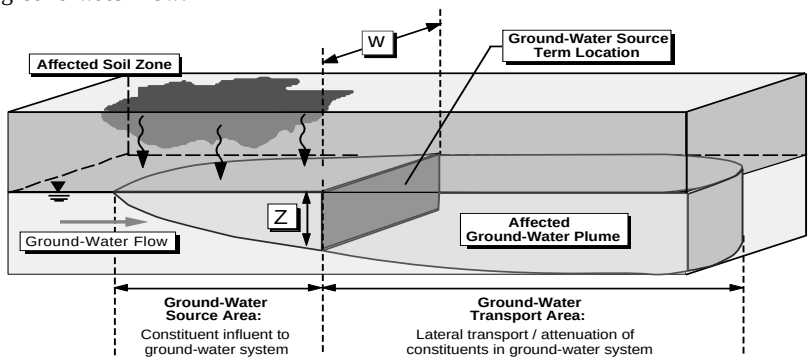
Parameter	***Model Area Length and Width (L and W)***
Units	ft
Description	Physical dimensions (in feet) of the rectangular area to be modeled. To determine contaminant concentrations at a particular point along the centerline of the plume (a common approach for most risk assessments), enter this distance in the "Modeled Area Length" box and see the results by clicking on the "Run Centerline" button. If one is interested in more accurate mass calculations, make sure most of the plume is within the zone delineated by the Modeled Area Length and Width. Find the mass flux results using the "Run Array" button.
Typical Values	500-3000 ft (length) 250-1000 ft (width)
Source of Data	Values should be slightly larger than the final plume dimensions or should extend to the downgradient point of concern (e.g., point of exposure). If only the centerline output is used, the plume width parameter has no effect on the results.
How to Enter Data	Enter directly.

Parameter	***Simulation Time (t)***
Units	years
Description	Time (in years) for which concentrations are to be calculated. For steady-state simulations, enter a large value (i.e., 1000 years would be sufficient for most sites).
Typical Values	1 to 1000 years
Source of Data	To match an existing plume, estimate the time between the original release and the date the field data were collected. To predict the maximum extent of plume migration, increase the simulation time until the plume no longer increases in length.
How to Enter Data	Enter directly.

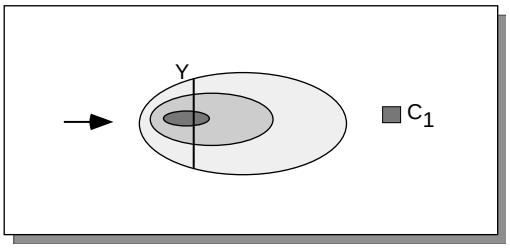
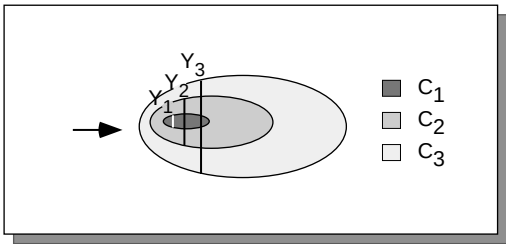
5. General Data, cont.

Parameter	*Zone 1 Length and Zone 2 Length*
Units	ft
Description	Lengths of first and second biotransformation zones in feet. The zone 1 length is the same as the model length if the user is modeling the plume as one zone. Modeling a site using two zones allows the user to specify different first order decay coefficients for each zone of the aquifer. One biotransformation zone is appropriate for sites where the environmental conditions (D.O., ORP, hydrogen concentrations etc.) do not change appreciably over the extent of the plume. For sites where environmental conditions change significantly over the extent of the plume, a 2-zone model may be more appropriate. For example, sites with high levels of fermentable organics (high H_2) near the source but not near the plume front may be best modeled in two zones because the concentration of hydrogen affects the the rate of reductive dechlorination. The hydrogen concentration, in turn, affects the first order decay coefficient. Although BIOCHLOR is primarily designed to model the anaerobic sequential decay of chlorinated solvents and no degradation zones, aerobic zones can also be modeled by experienced users (see Appendix A.2 for instructions). **Note that two-zone biotransformation estimates should only be used when the plumes in zone 1 are at steady-state (i.e., concentrations not changing with time). Refer to Appendix A.2 for a more detailed discussion.**
Typical Values	500-3000 ft
Source of Data	If only one biotransformation zone is being modeled, then use the same value as the model length. If the plume will be modeled in two zones, delineate the two zones by looking at field data (e.g., D.O. , fermentable carbon, hydrogen concentrations, etc.) and determine an appropriate distance from the source.
How to Enter Data	Enter the value for zone 1 directly. The value for zone 2 will be automatically calculated by deducting the zone 1 length from the model area length when the "C" button is pressed. If only one biotransformation zone is being modeled, be sure that the zone 1 length is the same as the model area length.

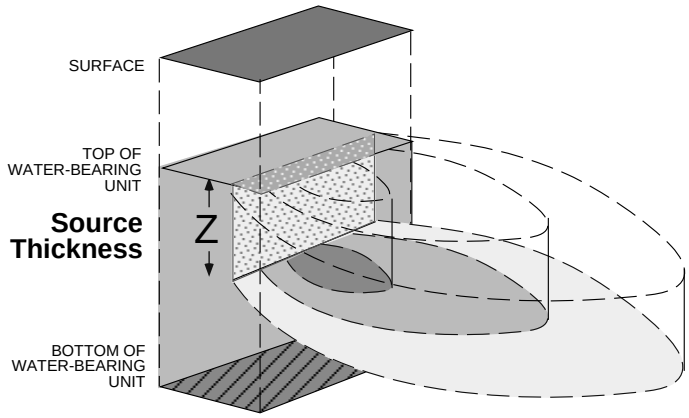
6. Source Data

Parameter	*Source Area Concentrations*
Units	mg/L
Description	Aqueous phase concentration of chlorinated solvents in the source area. The source term corresponds to a vertical source plane, normal to the direction of ground-water flow, located at the downgradient limit of the area serving as the principal source of solvent release to the ground water (e.g., affected unsaturated zone soils, NAPL plume, land disposal unit, spill area etc.). In the absence of such data, the source term should be located at the point of the maximum measured plume concentration(s). One "rule of thumb" for inferring the location of DNAPL is to look for aqueous phase concentrations in excess of 1% of solubility (Pankow and Cherry, 1995; Cohen and Mercer, 1993). Distance to downgradient points of exposure should then be measured from this location along the principal direction of ground-water flow.  For the single planar option, the maximum source area concentration should be entered on the input page (or in the dialog box that transfers the data to the input page). For the spatially-varying option, the user may enter three concentrations. The maximum concentration in the source area can be used in area 1 and geometric mean concentrations can be used in areas 2 and 3. Using a single planar source yields accurate centerline concentration profiles, but concentrations off the centerline will be overestimated. The use of a spatially variable source will yield better off-centerline concentration estimates but requires considerably more computation time. For centerline simulations, the single planar option is recommended.
Typical Values	0.010 to 120 mg/L Note: Source area dissolved solvent concentrations should not exceed the aqueous solubility at a given temperature. The following are the aqueous phase solubilities at 20 °C (Mackay *et al*., 1993): PCE 150 mg/L; 1,1,1-TCA 4400 mg/L TCE 1100 mg/L; 1,1-DCA 5500 mg/L cDCE 800 mg/L; CA 5710 mg/L VC 6800 mg/L
Source of Data	Source area monitoring well data
How to Enter Data	Enter directly on input page or press "Source Options" button and follow instructions.

6. Source Data, cont.

Parameter	***Source Area Width***
Units	ft
Description	The Domenico (1987) model assumes a vertical plane source of constant concentration. The source width is the extent of the source area perpendicular to the ground-water flow.
Typical Values	120-700 ft
Source of Data	To determine a source width across the site, draw a line perpendicular to the direction of ground-water flow direction in the source area. The source area is typically defined as being the area with contaminated soils having high concentrations of sorbed organics, free-phase NAPLs, or residual NAPLs. If the source area covers a large area, it is best to choose the most downgradient or widest point in the source area for determining the source width. Single Planar For a single planar source, choose one width.  Spatially-Varying For a spatially variable source, BIOCHLOR allows the user to enter up to three widths and concentrations to define the source area using isopleth data. See the diagram below. 
How to Enter Data	Enter directly on input page or press “Source Options” button and follow instructions.

6. Source Data, cont.

Parameter	*Source Thickness In Saturated Zone (Z)*
Units	ft
Description	Thickness of dissolved solvent in the source area The Domenico (1987) model assumes a vertical plane source of constant concentration. For many solvent spill sites the thickness of this source area will be the saturated thickness of the aquifer. As these solvents sink to the bottom of the aquifer, they leave residual DNAPL behind that act as a source of ground-water contamination that extends vertically from the water table to the bottom of the saturated zone. 
Typical Values	20-50 ft
Source of Data	This value is usually determined by evaluating ground-water data from wells near the source area screened at different depths. If this type of information is not available, then the depth of the aquifer can be used as a conservative estimate.
How to Enter Data	Enter directly.

7. Field Data for Comparison

Parameter	*Field Concentrations (and Distances from Source)*
Units	mg/L
Description	These parameters are concentrations of dissolved organics in wells near the centerline of the plume. These data are used to help calibrate the model and are displayed with model results in the "Run Centerline" option.
Typical Values	0.001 to 50 mg/L
Source of Data	Monitoring wells located near the centerline of the plume.
How to Enter Data	Enter as many or as few of these points as needed. The data are used only to help calibrate the model when comparing the results from the centerline option. Enter the distance from the source that corresponds to the field concentration. ***Warning: Do NOT cut and paste field data from one column to another. This can cause spreadsheet errors. Copy data and then erase unwanted data.***

Analyzing BIOCHLOR Output

The output shows concentrations along the centerline (for two kinetic models at the same time) or as an array (one kinetic model at a time). Note that all results are for the time entered in the "Simulation Time" box.

Centerline Output

Centerline output is displayed when the “Run Centerline” button is pressed on the input screen. The centerline output screen shows the concentration at the top of the saturated zone (z=0) along the centerline of the plume (y=0). The first screen shows the concentration profiles and field data for all the constituents on one plot as well as a no degradation curve for the total chlorinated solvents. This information is plotted on a linear plot. The user may view the output on a semi-log plot by pressing the “Log <—> Linear” button.

On the second output screen, the user can view the no degradation curves and the biotransformation curves for each constituent one at a time by pressing the buttons to the right. The model predictions are also presented in tabular form and may be printed out.

After a simulation has been run and the user has returned to the input page, the user may opt to use the “See Output” button. This button allows the user to go directly to the output without running the model. If the “See Output” button is pressed prior to running a simulation, output errors may result.

Array Output

The array output is displayed when the “Run Array” button is pressed on the Input screen. Choose the constituent that you would like to view by selecting it in the upper right hand corner. Then select one of the two model types (No Degradation or Biotransformation). A 3-D graphic presents the concentration profile on an 11-point-long by 5-point-wide grid. To alter the modeled area, adjust the Model Area Length and Width parameters on the input screen.

To see the plume array that exceeds a certain target level (such as an MCL or risk-based cleanup level), enter the target level in the box and push "Plot Data > Target". Only sections of the plume exceeding the target level will be displayed. To see all the data again, push "Plot All Data". Note that BIOCHLOR automatically resets this button to "Plot All Data" when the "Run Array" button is pressed on the input screen. Approximate mass flux data are presented on the array output screen.

Calculating the Mass Balance (Order-of-Magnitude Accuracy)

Plume Mass (kg)
BIOCHLOR calculates the mass of organics in the plume array for two models: 1) No Degradation and 2) Sequential First Order Decay (Biotransformation/Production) The mass is calculated by assuming that each point represents a cell equal to the incremental width and length (except for the first column which is assumed to be half as long as the other columns because the source is assumed to be in the middle of the cell). The volume of the affected ground water in each cell is calculated by multiplying the area of each cell by the source depth and by effective porosity (the mass balance calculation assumes 2-D transport). The mass of organics in each cell is then determined by multiplying the volume of ground water by the concentration and then by the retardation factor to account for sorbed constituents.

Mass Removed (kg), % Biotransformed, and % Change in Mass Flux
The mass removed is the difference between the mass of contaminant if no biotransformation occurs and the mass of contaminant if biotransformation/productions occurs. For some daughter products, the mass removed may be negative as more mass is created than would be present if no biotransformation occurred. The percent biodegraded is the mass of solvent removed divided by the mass of solvent if no biotransformation occurs. The percent change in mass flux is the difference in mass flux at the source compared to the mass flux at the boundary of the model area.

Current Volume of Ground Water in Plume (ac-ft)

BIOCHLOR counts the number of cells in the 5 x 10 array with concentration values greater than 0, and multiplies this by the volume of ground water in each cell (length * width * source thickness * effective porosity).

If the user wishes to estimate the volume of the plume above a certain target level, enter the target level in the appropriate box and press the appropriate model (No Degradation or Biotransformation) to display the result.

Note that the model does not account for any effects of vertical dispersion.

If BIOCHLOR Says "Can't Calc." for Volume

If the contaminant concentration in the plume at the end of the model length is greater than 0.005 mg/L , then the model concludes that the model area (see Input Screen, Section 5: General Data) is not sized to capture the entire plume volume in the 5x10 array and writes "Can't Calc" in the box. The user is encouraged to adjust the modeled length and width to capture the plume in the 5x10 array.

Flow Rate of Water Through Source Area (ac-ft/yr)

Using the Darcy velocity, the source thickness, and the source width, BIOCHLOR calculates the rate that clean ground water moves through the source area where it will pick up dissolved solvents. Note that the ground-water Darcy velocity is equal to the ground-water seepage velocity multiplied by effective porosity.

Quick Start

Minimum System Requirements

The BIOCHLOR model requires a computer system capable of running Microsoft© Excel 7.0 or '97 for Windows. If you have Excel '97, you are advised to use the Excel '97 version of BIOCHLOR. Operation requires an IBM-compatible PC equipped with a Pentium or later processor running at a minimum of 150 MHz. A minimum of 32 MB of system memory (RAM) is strongly recommended.

Installation and Start-Up

The software is installed by copying the BIOCHLOR model file (BIOCHL7.xls or BIOCH97.xls) and the BIOCHLOR help file (BIOCHLR.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. If you are using Excel '97, 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.

BIOCHLOR 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 ("pop-up window") then the dialog box will close. Do not press "Enter" and move to the next cell by using the mouse and clicking. 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 to create 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, BIOCHLR.HLP. 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 BIOCHLR.HLP, and it was installed in the same directory/folder as the BIOCHLOR model file (BIOCHL7.xls or BIOCH97.xls).
- 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.

- Change the WinHelp call in the VB Module to “hard code” the directory information. That way, the file name and its full path will be explicitly passed to WinHelp. If you have Excel 7.0, go to Tools and select Options. From Options, select the View tab and check sheet tabs. You will then see the worksheet tabs. Select the Macro Module tab and search for the text “Helpfile”. Enter the new path. If you have Excel ‘97, 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.
- 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

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Appendix A.1

Domenico Single Species Analytical Model

Domenico (1987) developed a semi-analytical solution for reactive transport with first order decay and a two-dimensional (i.e., planar) source geometry. BIOCHLOR uses the Domenico solution with Martin-Hayden and Robbins (1997) improvements and assumes that degradation reactions occur only in the aqueous phase. BIOCHLOR evaluates centerline concentrations at y=0, z=0 and the 2-D array at z=0. The model equation, boundary conditions, assumptions, and limitations are discussed below.

Domenico Model with First Order Decay

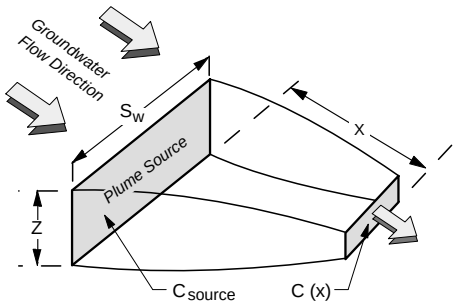
$$C(x,y,z,t) = \frac{C_O}{8} f_x f_y f_z$$

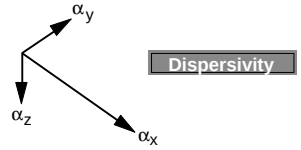
$$f_x = \exp\left(\frac{x\left[1-\left(1+4\lambda\alpha_x/v_s\right)^{0.5}\right]}{2\alpha_x}\right) * erfc\left(\frac{x - vt\left(1+4\lambda\alpha_x/v_s\right)^{0.5}}{2\left(\alpha_x vt\right)^{0.5}}\right) +$$

$$\exp\left(\frac{x\left[1+\left(1+4\lambda\alpha_x/v_s\right)^{0.5}\right]}{2\alpha_x}\right) * erfc\left(\frac{x + vt\left(1+4\lambda\alpha_x/v_s\right)^{0.5}}{2\left(\alpha_x vt\right)^{0.5}}\right)$$

$$f_y = \text{erf}\left(\frac{(y+Y/2)}{2\left(\alpha_y x\right)^{0.5}}\right) - \text{erf}\left(\frac{(y-Y/2)}{2\left(\alpha_y x\right)^{0.5}}\right) \qquad f_z = \text{erf}\left(\frac{z+Z}{2\left(\alpha_z x\right)^{0.5}}\right) - \text{erf}\left(\frac{(z-Z)}{2\left(\alpha_z x\right)^{0.5}}\right)$$

Definitions





C(x, y, z, t)	Concentration at distance x downstream of source and distance y off centerline of plume at time t (mg/L)
Co	Concentration in Source Area at t=0 (mg/L)
x	Distance downgradient of source (ft)
y	Distance from plume centerline of source (ft)
z	Distance from top of saturated zone to measurement point (assumed to be 0; concentration is always given at top of saturated zone).
α_x	Longitudinal ground-water dispersivity (ft)
α_y	Transverse ground-water dispersivity (ft)
α_z	Vertical ground-water dispersivity (ft)
θ_e	Effective Soil Porosity
λ	First-Order Degradation Rate Coefficient(day^{-1})
v_s	Seepage Velocity (ft/yr)=Ki/(θ_e)
v	Chemical Velocity (ft/yr)=v_s/R
K	Hydraulic Conductivity (ft/yr)
R	Constituent retardation factor
i	Hydraulic Gradient (cm/cm)
Y	Source Width (ft)
Z	Source Depth (ft)

Note that because biotransformation is assumed to occur only in the aqueous phase, the first order rate constant, λ, has been divided by R. However, R can be canceled out by replacing v (the compound velocity (i.e., v_s/R)) in the original Domenico solution with $v_{s,}$ (the seepage velocity).

The Domenico solution was modified for chloroethane (CA) reactive transport to take into consideration both biotic and abiotic reactions. The first order rate constant for abiotic decay, λ_A, is added to the biological rate constant for reductive dechlorination, λ, as shown below. All other terms in the Domenico equation remain the same.

$$f_x = \exp\left(\frac{x\left[1-\left(1+4(\lambda+\lambda_A)\alpha_x / v_s\right)^{0.5}\right]}{2\alpha_x}\right) * \operatorname{erfc}\left(\frac{x-vt\left(1+4(\lambda+\lambda_A)\alpha_x / v_s\right)^{0.5}}{2\left(\alpha_x vt\right)^{0.5}}\right) +$$

$$\exp\left(\frac{x\left[1+\left(1+4(\lambda+\lambda_A)\alpha_x / v_s\right)^{0.5}\right]}{2\alpha_x}\right) * \operatorname{erfc}\left(\frac{x+vt\left(1+4(\lambda+\lambda_A)\alpha_x / v_s\right)^{0.5}}{2\left(\alpha_x vt\right)^{0.5}}\right)$$

The initial conditions of the Domenico model are:

1. $c(x, y, z, 0) = 0$ (Initial concentration = 0 for x, y, z, > 0)
2. $c(0, Y, Z, 0) = C_0$ (Source concentration for each vertical plane source = C_0 at time 0)

The key assumptions in the model are:

1. The aquifer and flow field are homogenenous 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.

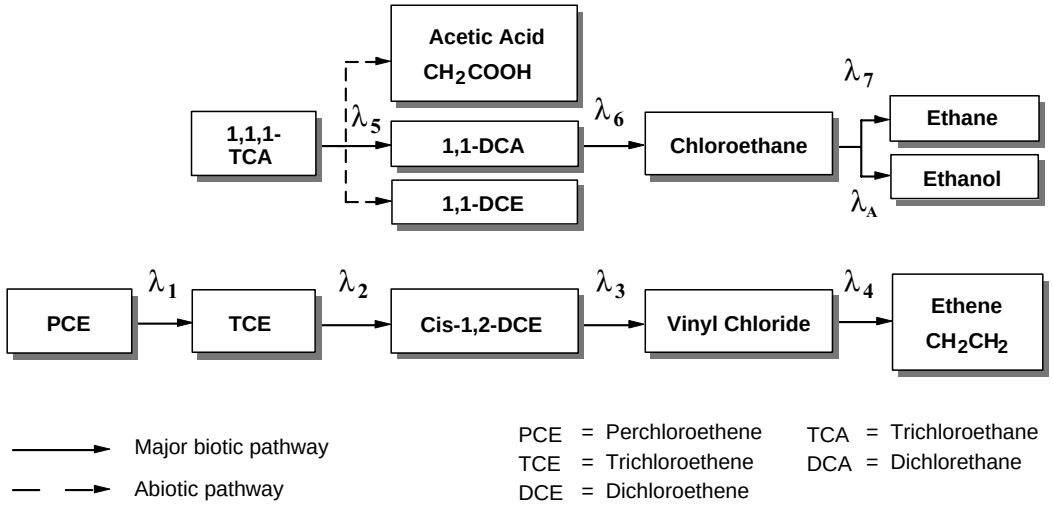
The most important modifications to the original Domenico model are:

1. 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.
2. 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.

Appendix A.2

Kinetics of Sequential First Order Decay

BIOCHLOR primarily models reductive dechlorination, which is assumed to follow sequential first order kinetics. The user may model the sequential decay of chlorinated ethenes, such as PCE and TCE, or the decay of chlorinated ethanes, such as 1,1,1-TCA, as shown below (Vogel and McCarty, 1987):



Although the chlorinated ethenes primarily degrade biologically, chlorinated ethanes can degrade both biologically and abiotically. BIOCHLOR allows the user to input both biological and abiotic rate constants for chloroethane. For chloroethane (CA), abiotic decay to ethanol occurs much more rapidly than biotransformation to ethane. The abiotic decay of 1,1-DCA is slow relative to biotransformation so its abiotic degradation is ignored in BIOCHLOR. 1,1,1-TCA can degrade abiotically to both acetic acid (by hydrolysis) and to 1,1-DCE (by elimination)(Vogel and McCarty, 1987). Abiotic decay of 1,1,1-TCA cannot be modeled using BIOCHLOR if accurate chlorinated ethane daughter product predictions are required. However, if only TCA predictions are needed, a lumped rate coefficient (sum of abiotic and biotic first order rate coefficients) can be input to model the degradation of TCA alone.

Chlorinated Ethenes

The reaction rate equations describing the sequential first order decay of the chlorinated ethenes are shown below :

$$r_{PCE} = -\lambda_1 C_{PCE}$$

$$r_{TCE} = y_1 \lambda_1 C_{PCE} - \lambda_2 C_{TCE}$$

$$r_{DCE} = y_2 \lambda_2 C_{TCE} - \lambda_3 C_{DCE}$$

$$r_{VC} = y_3 \lambda_3 C_{DCE} - \lambda_4 C_{VC}$$

$$r_{ETH} = y_4 \lambda_4 C_{VC} - \lambda_5 C_{ETH}$$

where λ_1,λ_2, λ_3, λ_4, and λ_5 are the first order biotransformation rate coefficients, y_1, y_2, y_3, y_4 are the daughter:parent compound molecular weight ratios, and C_{PCE}, C_{TCE}, C_{DCE}, C_{VC} and C_{ETH} are the aqueous concentration of PCE, TCE, DCE, vinyl chloride, and ethene, respectively. (Note: BIOCHLOR assumes no degradation of ethene (λ_5=0) in zone 1.) From these expressions, it is clear that TCE, DCE, and VC are simultaneously being produced and degraded, which

often results in net accumulation before observed degradation. Furthermore, these reaction expressions cause the reactive transport equations to be coupled to each other as discussed in more detail in Appendix A.3.

Chlorinated Ethanes

The following are the rate expressions for the degradation of the chlorinated ethanes.

$$r_{TCA} = -\lambda_5 C_{TCA}$$

$$r_{DCA} = y_5 \lambda_5 C_{TCA} - \lambda_6 C_{DCA}$$

$$r_{CA} = y_6 \lambda_6 C_{DCA} - (\lambda_7 + \lambda_A) C_{CA}$$

where λ_5,λ_6 and λ_7 are the biotransformation rate coefficients, λ_A is the abiotic rate coefficients for chloroethane, y_5 and y_6 are the daughter:parent compound molecular weight ratios and C_{TCA}, C_{DCA} and C_{CA} are the concentration of 1,1,1-trichloroethane, 1,1-dichloroethane and chloroethane, respectively.

Because BIOCHLOR is programed in mass units, yield constants (i.e., y_1, y_2,...y_6) to account for molecular weight differences between parent and daughter compounds were incorporated. The constants are necessary because kinetic expressions are valid on a molar basis only.

Other Chlorinated Compounds

Although BIOCHLOR is programmed to model the reductive dechlorination of chlorinated ethenes and ethanes primarily, it can also be used to model any chlorinated compound that degrades via sequential first order decay kinetics. To use BIOCHLOR for compounds other than chlorinated ethenes and ethanes, the user must input the yield constants (the ratio of daughter product to parent compound molecular weights on the input page). Be aware that output graphs will still show the chlorinated ethene or ethane labels.

1-Zone vs. 2 -Zone Biotransformation

If the contaminant plumes are at **steady-state**, BIOCHLOR can be used to model the plume in two zones with a different set of biotransformation rate coefficients in each zone. BIOCHLOR is primarily designed to handle zones with anaerobic degradation and no degradation, but it can be manipulated by experienced users to accommodate an aerobic zone in zone 2 in some cases. BIOCHLOR cannot model aerobic conditions in zone 1. Table A.1 presents the scenarios that BIOCHLOR can execute. A “Type I” environment occurs when the primary substrate is anthropogenic carbon (e.g., BTEX or landfill leachate) and microbial fermentation of this anthropogenic carbon produces dissolved hydrogen that drives reductive dechlorination. A “Type II” environment occurs in areas with high concentrations of biologically available native organic carbon. The microbial utilization of the native organic carbon produces dissolved hydrogen which drives reductive dechlorination. A Type III environment occurs in areas characterized by low concentrations of both anthropogenic and natural organic carbon and an oxygen concentration greater than 1.0 mg/L (USEPA, 1998). For all two-zone simulations, a single (fixed) longitudinal dispersivity value must be used for both zones.

Table A.1. 2-Zone Biotransformation Scenarios

Scenario	***Zone 1***	***Zone 2***
1	Type I or II (anaerobic, high rates)	Type I or II (anaerobic, lower rates or no degradation)
2	No Degradation	Type I or II
3	Type I or II	Type III

Scenario 3 is illustrated in Figure A.1. Here, all the solvents degrade anaerobically in zone 1 but only VC , c-DCE, and ETH degrade to carbon dioxide under aerobic conditions in zone 2.

In modeling scenario 3 for the chlorinated ethenes, it may be necessary to carry out three separate simulations to generate concentration profiles for all of the chlorinated solvents and ethene. Multiple simulations are necessary because the equations programmed in BIOCHLOR incorporate sequential first order kinetics expressions and therefore link dissolved solvent degradation with daughter product generation. Under aerobic conditions, the solvent is assumed to degrade directly to carbon dioxide via first order kinetics, and degradation is not linked to daughter product generation. Input parameters can be manipulated to avoid accounting for daughter product generation. **The user should be aware that BIOCHLOR is primarily designed to display the original anaerobic pathways. The input/output will not**

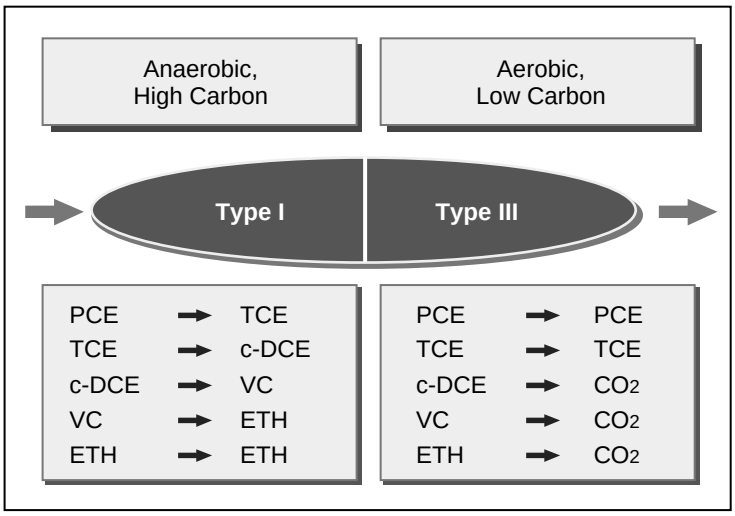


Figure A.1. Mixed type I/Type III plume conditions.

indicate that an aerobic path was used or what the degradation products are. The user should extract only the pertinent output information using the guidance below.

Table A.2 outlines how to input rate constants for both zones (anaerobic zone 1 and aerobic zone 2) for each simulation. Rate constants denoted as λ' indicate a rate constant for an aerobic process. Note that the rate of ethene degradation under anaerobic conditions in zone 1 is assumed to be zero. If only c-DCE degrades under aerobic conditions, then scenario 3 can be completed in one run. If c-DCE, VC and ETH degrade aerobically, three runs will be required. Run 1 will yield the concentration profiles for PCE, TCE, and c-DCE. (Concentration profiles for VC and ETH must be ignored). Run 2 will yield the concentration profiles for VC. (Concentration profiles for all other compounds must be ignored.) Run 3 will yield the concentration profile for ethene (again, concentration profiles for all other compounds must be ignored). The clearest way to present this data is to transfer data from each run to a new Excel spreadsheet and re-plot.

Table A.2. Modeling scenario 3 for chlorinated ethenes.

Compound	***Run 1***		***Run 2***		***Run 3***	
	Zone 1	**Zone 2**	**Zone 1**	**Zone 2**	**Zone 1**	**Zone 2**
PCE	λ_1	0	λ_1	0	λ_1	0
TCE	λ_2	0	λ_2	0	λ_2	0
DCE	λ_3	λ_3'	λ_3	0	λ_3	0
VC	λ_4	0	λ_4	λ_4'	λ_4	0
ETH	0	0	0	0	0	λ_5'

Shaded boxes indicate compounds whose output data should be recorded during each run.

For the chlorinated ethanes, chloroethane is the only solvent that is degraded aerobically so that scenario 3 can be accomplished with one run as outlined in Table A.3.

Table A.3: Modeling Scenario 3 for Chlorinated Ethanes

Compound	*Run 1*	
	Zone 1	Zone 2
TCA	λ_1	**0**
1,1-DCA	λ_2	**0**
CA	λ_3	λ_3'

How BIOCHLOR Models 2-Zone Biotransformation

The Domenico solution was developed assuming a constant source concentration and a constant biotransformation rate coefficient. Simply changing the value of the rate constant at the boundary between zones 1 and 2 yields a large discontinuity in the concentration profile. Therefore, a new "source" area was defined at the boundary of zones 1 and 2. The new source was defined using the concentrations in the last cells of the zone 1 array and modeled as a spatially-variable source. To test the validity of this approach, two simulations were carried out. In the first, the model length was modeled as one zone of 1200 ft. In the second simulation, the model length was divided into two zones (200 ft for zone 1 and 1000 ft for zone 2) and the biological rate constants that were used in the 1-zone simulation were used in each zone of the 2-zone simulation. These simulations were carried out at steady state. These simulations show that this solution technique yields good concentration estimates when the plume is at steady state (Figure A.2). The steady-state condition is required to ensure that the concentrations are constant at the boundary between the two zones. **The use of the 2-zone biotransformation model should NOT be used when the plume is not at steady-state throughout zone 1.**

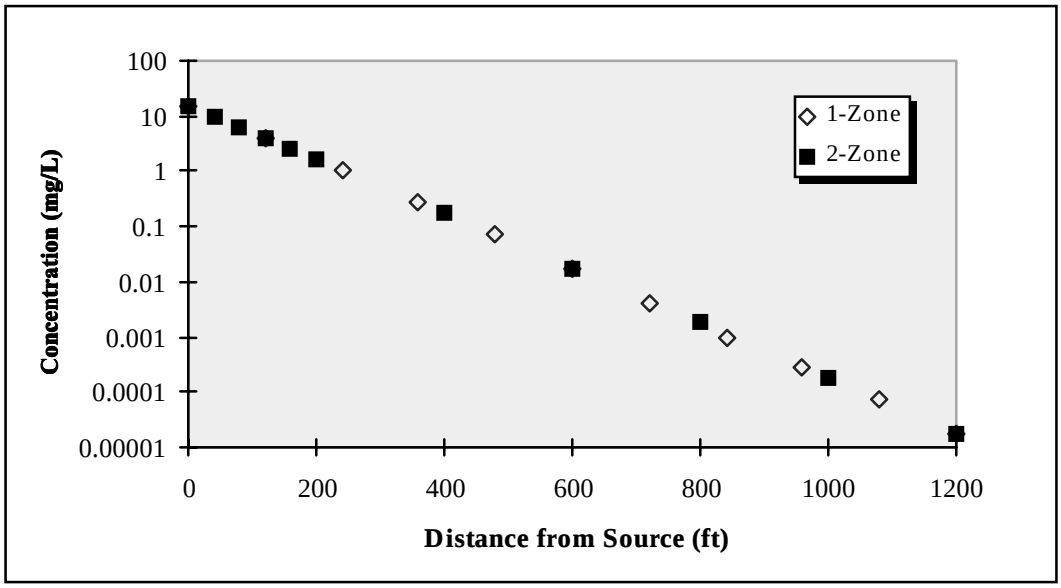


Figure A.2. Comparison of solution techniques for BIOCHLOR 1-zone and 2-zone biotransformation models.

Appendix A.3

BIOCHLOR Solution

By T. Prabhakar Clement and Yunwei Sun, Battelle Pacific Northwest National Laboratory, Richland, WA 99345.

Governing Equations

The BIOCHLOR software solves a set of coupled partial differential equations to describe the reactive transport of chlorinated solvent species, such as PCE, TCE, DCE, VC and ETH, in saturated ground-water systems. The equations describe one-dimensional advection, three-dimensional dispersion, linear sorption, and sequential, first-order biotransformation. All equations, except the first, are coupled to a parent species equation through the reaction term as shown below:

$$R_1 \frac{\partial c_1}{\partial t} = D_x \frac{\partial^2 c_1}{\partial x^2} + D_y \frac{\partial^2 c_1}{\partial y^2} + D_z \frac{\partial^2 c_1}{\partial z^2} - v_s \frac{\partial c_1}{\partial x} - k_1 c_1 \quad (1)$$

$$R_2 \frac{\partial c_2}{\partial t} = D_x \frac{\partial^2 c_2}{\partial x^2} + D_y \frac{\partial^2 c_2}{\partial y^2} + D_z \frac{\partial^2 c_2}{\partial z^2} - v_s \frac{\partial c_2}{\partial x} + y_1 k_1 c_1 - k_2 c_2 \quad (2)$$

$$R_3 \frac{\partial c_3}{\partial t} = D_x \frac{\partial^2 c_3}{\partial x^2} + D_y \frac{\partial^2 c_3}{\partial y^2} + D_z \frac{\partial^2 c_3}{\partial z^2} - v_s \frac{\partial c_3}{\partial x} + y_2 k_2 c_2 - k_3 c_3 \quad (3)$$

$$R_4 \frac{\partial c_4}{\partial t} = D_x \frac{\partial^2 c_4}{\partial x^2} + D_y \frac{\partial^2 c_4}{\partial y^2} + D_z \frac{\partial^2 c_4}{\partial z^2} - v_s \frac{\partial c_4}{\partial x} + y_3 k_3 c_3 - k_4 c_4 \quad (4)$$

$$R_5 \frac{\partial c_5}{\partial t} = D_x \frac{\partial^2 c_5}{\partial x^2} + D_y \frac{\partial^2 c_5}{\partial y^2} + D_z \frac{\partial^2 c_5}{\partial z^2} - v_s \frac{\partial c_5}{\partial x} + y_4 k_4 c_4 - k_5 c_5 \quad (5)$$

where c_1, c_2, c_3, c_4, and c_5 are concentrations of PCE, TCE, DCE, VC, and ETH, respectively [mg/L]; D_x, D_Y, and D_Z are the hydrodynamic dispersion coefficients [ft²/yr]; v_s is the seepage velocity [ft/yr]; k is the first-order degradation coefficient [1/yr]; y is the yield coefficient [a dimensionless value; for example, y_1 would represent the mg of TCE produced per unit mg of PCE destroyed]; and R_1, R_2, R_3, R_4, and R_5 are respective retardation factors. In BIOCHLOR, the retardation factor values of different species are averaged to compute an "effective retardation factor, R", which is in turn used to compute the effective transport velocity and dispersion coefficients. Also, biotransformation is assumed to occur only in the aqueous phase (which is a conservative assumption) and hence R is used to divide all the degradation reaction terms.

Analytical Solution Strategy

The Domenico (1987) solution with some minor improvements suggested by Martin-Hayden and Robbins (1997) was used as the base solution to solve the three dimensional problem. The solution was directly used to solve the independent equation 1. However, since equations 2 to 5 are coupled equations, the Domenico solution cannot be used to solve them. Therefore, in BIOCHLOR a new transformation procedure is used to first uncouple equations 2 to 5 and recast them in the form of equation 1 (Sun and Clement, 1999; Sun et al. 1999a, Sun et al. 1999b). The transformation equations used are:

$$a_2 = c_2 + \frac{y_1 k_1}{k_1 - k_2} c_1 \quad (6)$$

$$a_3 = c_3 + \frac{y_2 k_2}{k_2 - k_3} c_2 + \frac{y_1 y_2 k_1 k_2}{(k_1 - k_3)(k_2 - k_3)} c_1 \quad (7)$$

$$a_4 = c_4 + \frac{y_3 k_3}{k_3 - k_4} c_3 + \frac{y_2 y_3 k_2 k_3}{(k_2 - k_4)(k_3 - k_4)} c_2 + \frac{y_1 y_2 y_3 k_1 k_2 k_3}{(k_1 - k_4)(k_2 - k_4)(k_3 - k_4)} c_1 \tag{8}$$

$$a_5 = c_5 + \frac{y_4 k_4}{k_4 - k_5} c_4 + \frac{y_3 y_4 k_3 k_4}{(k_3 - k_5)(k_4 - k_5)} c_3 + \frac{y_2 y_3 y_4 k_2 k_3 k_4}{(k_2 - k_5)(k_3 - k_5)(k_4 - k_5)} c_2 + \frac{y_1 y_2 y_3 y_4 k_1 k_2 k_3 k_4}{(k_1 - k_5)(k_2 - k_5)(k_3 - k_5)(k_4 - k_5)} c_1 \tag{9}$$

It can be shown that using transformation equations 6 to 10, the reactive transport equations 2 to 5 can be written in a transformed “a” domain where the coupled transport equations reduce to a form similar to equation 1. For illustration purposes, the steps involved in proving the strategy for a one-dimensional, 2-species transport problem are given below.

Consider the following set of one-dimensional fate and transport equations that describe two reacting species that are coupled by first-order decay reactions:

$$\frac{\partial c_1}{\partial t} = D_x \frac{\partial^2 c_1}{\partial x^2} - v \frac{\partial c_1}{\partial x} - k_1 c_1 \tag{10}$$

$$\frac{\partial c_2}{\partial t} = D_x \frac{\partial^2 c_2}{\partial x^2} - v \frac{\partial c_2}{\partial x} + y_1 k_1 c_1 - k_2 c_2 . \tag{11}$$

Since equation 10 is already in the standard form, it can be solved using a standard analytical solution. Based on Sun et al. (1999a) work, a transformation for the second equation can be written as:

$$a_2 = c_2 + \frac{y_1 k_1}{k_1 - k_2} c_1 . \tag{12}$$

Differentiating equation 12 partially with respect to time we get,

$$\frac{\partial a_2}{\partial t} = \frac{\partial c_2}{\partial t} + \frac{y_1 k_1}{k_1 - k_2} \frac{\partial c_1}{\partial t} \tag{13}$$

Substituting (10) and (11) into (13) we get,

$$\frac{\partial a_2}{\partial t} = D_x \frac{\partial^2 c_2}{\partial x^2} - v \frac{\partial c_2}{\partial x} + y_1 k_1 c_1 - k_2 c_2 + \frac{y_1 k_1}{k_1 - k_2} \left[D_x \frac{\partial^2 c_1}{\partial x^2} - v \frac{\partial c_1}{\partial x} - k_1 c_1 \right] \tag{14}$$

Equation 14 can be rearranged as,

$$\frac{\partial a_2}{\partial t} = D_x \frac{\partial^2}{\partial x^2} \left[c_2 + \frac{y_1 k_1}{k_1 - k_2} c_1 \right] - v \frac{\partial}{\partial x} \left[c_2 + \frac{y_1 k_1}{k_1 - k_2} c_1 \right] + y_1 k_1 c_1 - k_2 c_2 + \frac{y_1 k_1^2 c_1}{k_1 - k_2} . \tag{15}$$

Using (12), equation 15 can be written as:

$$\frac{\partial a_2}{\partial t} = D_x \frac{\partial^2 a_2}{\partial x^2} - v \frac{\partial a_2}{\partial x} - k_2 c_2 + y_1 k_1 c_1 - \frac{y_1 k_1^2 c_1}{k_1 - k_2} . \tag{16}$$

Combining the last three terms, equation 16 can be simplified to:

$$\frac{\partial a_2}{\partial t} = D_x \frac{\partial^2 a_2}{\partial x^2} - v \frac{\partial a_2}{\partial x} - k_2 a_2 . \tag{17}$$

To solve (11), first a standard, one-dimensional solution should be used to solve (17) for computing a_2 values and to solve (10) for computing c_1 values (note that c_1 is always same as a_1). Then, c_2 values can be computed using equation 12 in an inverse mode. This procedure can be repeated for solving any number of coupled reactive species. A more general analysis of this solution strategy, and a detailed comparison of the analytical results against the numerical results of the RT3D code are discussed in Sun and Clement (19998).

If retarding species are assumed then an effective retardation factor is used to divide the transport velocity, dispersion coefficients and degradation rates (since degradation is assumed to occur only in the aqueous phase). It should be noted that the proposed analytical solution strategy would work only when the constant effective retardation factor is used to represent the retardation characteristics of all the transported species.

Computational Procedure

In BIOCHLOR, the initial concentration of all the species is assumed to be zero. The boundary conditions at the source location can be non zero for one or more of the species. The first step involved in applying the solution strategy is to convert all initial and boundary conditions of all daughter species into the transformed ("a") domain using the transformation equations 6 to 9. After transforming all initial and boundary conditions, the Domenico solution is used five times to prepare the solution array "a" (a_i values at all nodes for all five species), in the transformed domain. Finally, the solution arrays are transformed back into the concentration domain ("c" domain) using an inverse form transformation equations 6 to 9. The FORTRAN code given below shows the implementation procedure:

```
C     Modeling Coupled PCE,TCE,DCE,VC and ETH Transport and Degradation in
C     3-Dimensional Ground-water Aquifers
C     This Fortran code was developed by: T.P. Clement & Y. Sun
C     Battelle Pacific Northwest National Laboratory.
      PARAMETER(nx=60, ny=31, nc=5)
c     ny should always be an odd number
      REAL*4 k
      DIMENSION c(nx,ny,nc),a(nx,ny,nc),k(nc),y(nc),c0(nc),a0(nc)
c     Input data for Martin-Hayden and Robbins test problem
c     Reference: Vol 35(2), p.339, Groundwater,1997.
       dx = 20.0    !delta x
       dy = 20.0    !delta y
       t = 33.0     !total simulation time (years)
       reta = 5.3   !effective retardation factor
       v = 111.7/reta !velocity (ft/yr)
       ax = 16.4      !alpha x (ft)
       ay = 1.64      !alpha y (ft)
       az = 0.0       !alpha z
       xsdim = 0.0    !source dimensions
       ysdim = 100.0
       zsdim = 10.0
c      Automatically set source locations
       xsloc = 0.0  !source x location is fixed at the left boundary
       ysloc = (((ny-1)/2)+1)*dy !fix source y location at the grid center
c     Input reaction parameters
           k(1) = 2.0/reta  !effective pce decay rate (1/yr)
           k(2) = 1.5/reta  ! tce decay rate
           k(3) = 0.8/reta  ! dce decay rate
           k(4) = 0.65/reta ! vc decay rate
       k(5) = 0.000000001 !ethene decay rate
           y(1) = 0.79492 ! ytce/pce
           y(2) = 0.73744 ! ydce/tce
           y(3) = 0.64499 ! yvc/dce
y(4) = 0.4496  !yeth/vc
c     Input source concentrations
           c0(1) = 0.1  !mg/l source concentration for pce
           c0(2) = 15.8 !for tce
           c0(3) = 98.5 !for dce
           c0(4) = 3.1  !for vc
c0(5) = 0.03 !for eth
c     Computing transformation coefficients
           p21 = y(1)*k(1)/(k(1)-k(2))
           p32 = y(2)*k(2)/(k(2)-k(3))
```

```
            p31 = y(1)*y(2)*k(1)*k(2)/((k(1)-k(3))*(k(2)-k(3)))
            p43 = y(3)*k(3)/(k(3)-k(4))
            p42 = y(2)*y(3)*k(2)*k(3)/((k(2)-k(4))*(k(3)-k(4)))
            p41 = y(1)*y(2)*y(3)*k(1)*k(2)*k(3)/
     $        ((k(1)-k(4))*(k(2)-k(4))*(k(3)-k(4)))
            p54 = y(4)*k(4)/(k(4)-k(5))
            p53 = y(3)*y(4)*k(3)*k(4)/((k(3)-k(5))*(k(4)-k(5)))
            p52 = y(2)*y(3)*y(4)*k(2)*k(3)*k(4)/
     $        ((k(2)-k(5))*(k(3)-k(5))*(k(4)-k(5)))
            p51 = y(1)*y(2)*y(3)*y(4)*k(1)*k(2)*k(3)*k(4)/
     $        ((k(1)-k(5))*(k(2)-k(5))*(k(3)-k(5))*(k(4)-k(5)))
c    Initial concentration is assumed to be zero for all species
c    Transform all boundary conditions into “a” domain
            a0(1) = c0(1)
            a0(2) = c0(2) + p21*c0(1)
            a0(3) = c0(3) + p32*c0(2) + p31*c0(1)
            a0(4) = c0(4) + p43*c0(3) + p42*c0(2) + p41*c0(1)
            a0(5) = c0(5) + p54*c0(4) + p53*c0(3) + p52*c0(2) +p51*c0(1)
c    Solve the problem using Domenico solution in the “a” domain
            DO ic = 1, nc
           CALL Domenico(nx,ny,dx,dy,t,xloc,ysloc,xsdim,ysdim,zsdim,v,
     $                  ax,ay,az,a0(ic),k(ic),a(1,1,ic))
            END DO
c   Transforming back into the “c” domain
c    Transform Species #1
            DO iy=1,ny
              DO ix=1,nx
                c(ix,iy,1) = a(ix,iy,1)
              END DO
            END DO
C    Transform Species #2
            DO iy=1,ny
              DO ix=1,nx
                c(ix,iy,2) = a(ix,iy,2) - p21*c(ix,iy,1)
               END DO
            END DO
c    Transform Species #3
            DO iy=1,ny
              DO ix=1,nx
                c(ix,iy,3) = a(ix,iy,3) - p32*c(ix,iy,2) - p31*c(ix,iy,1)
               END DO
            END DO
c    Transform Species #4
            DO iy=1,ny
              DO ix=1,nx
                c(ix,iy,4) = a(ix,iy,4) - p43*c(ix,iy,3)
     $                  - p42*c(ix,iy,2) - p41*c(ix,iy,1)
              END DO
            END DO
c    Transform Species #5
            DO iy=1,ny
              DO ix=1,nx
                c(ix,iy,5) = a(ix,iy,5) - p54*c(ix,iy,4)
     $        - p53*c(ix,iy,3) - p52*c(ix,iy,2) - p51*c(ix,iy,1)
              END DO
             END DO
c   Output concentration array
           OPEN(10,FILE=”conc.out”,FORM=’FORMATTED’,STATUS=’UNKNOWN’)
           DO ic = 1, nc
              Write (10,*) “Species# =”,ic
              DO i = 1, ny
                  WRITE(10,12) (c(j,i,ic),j=1,nx)
              ENDDO
           ENDDO
12         FORMAT (10e15.6)
```

```
c   Ouput centerline concentrations
        OPEN(12,FILE="center.out",FORM='FORMATTED',STATUS='UNKNOWN')
        i = (((ny-1)/2)+1) !center line location
        DO j = 1, nx
           WRITE(12,14) j*dx, (c(j,i,ic),ic=1,5)
        END DO
14      FORMAT(F10.2,5e15.5)
         STOP
         END

          SUBROUTINE  Domenico(nx,ny,dx,dy,t,xsloc,ysloc,xsdim,ysdim,
     $                    zsdim,v,ax,ay,az,c0,k,c)
          USE MSIMSL !using IMSL subroutine
          REAL*4 k
          DIMENSION c(nx,ny)
          DO j=1,ny
         DO i=1,nx
               c(i,j)=0.0
            ENDDO
          ENDDO
c Domenico Anlytical Solution is used as in Martin-Hayden and Robbins paper
c See equations 5 & 1 in GW vol.35(2), 1997, pages p.345 and 340.
       cc = SQRT(1.+(4.*k*ax/v))
        DO j=1,ny
             DO i=1,nx
    x=i*dx-xsloc
              y=j*dy-ysloc
              z= 0.0 !at the water table
           hx2=ERFC((x - v*t*cc)/(2*SQRT(ax*v*t)))
           IF (hx2 .LE. 1.0e-30) THEN
              h1 = 0.0
           ELSE
              hx1=EXP((x*(1.-cc))/(2.*ax))
              h1=hx1*hx2
           END IF
           hx4=ERFC((x + v*t*cc)/(2*SQRT(ax*v*t)))
           IF (hx4 .LE. 1.0e-30) THEN
              h2 = 0.0
                ELSE
              hx3=EXP((x*(1.+cc))/(2.*ax))
              h2=hx3*hx4
                END IF
           hx = h1+h2
               fy=ERF((y+ysdim/2.0)/(2.0*SQRT(ay*x)))
     $           -ERF((y-ysdim/2.0)/(2.0*SQRT(ay*x)))
              IF (az. LE .1.0e-30) THEN
                 fz=2.0
              ELSE
                  fz= ERF((z+zsdim)/(2.0*SQRT(az*x)))
     $             -ERF((z-zsdim)/(2.0*SQRT(az*x)))
              ENDIF
              c(i,j)=(c0/8.0)*hx*fy*fz
            END DO
           END DO
       RETURN
       END
```

Appendix A.4

Dispersivity Estimates

Dispersion refers to the process whereby a dissolved solvent will be spatially distributed longitudinally (along the direction of ground-water flow), transversely (perpendicular to ground-water flow), and vertically (downward) 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.

Selection of dispersivity values is a difficult process, given the impracticability of measuring dispersion in the field. However, dispersivity data from over 50 sites has been compiled by Gelhar *et al.* (1992) (see Figures A.3 and A.4). The empirical data indicates that longitudinal dispersivity, in units of length, is related to scale (distance between source and measurement point). Gelhar *et al.* (1992) indicate 1) there is a considerable range of dispersivity values at any given scale (on the order of 2 - 3 orders of magnitude), 2) suggest using values at the low end of the range of possible dispersivity values, and 3) caution against using a single relation between scale and dispersivity to estimate dispersivity. However, most modeling studies do start with such simple relations, and BIOCHLOR is programmed with some commonly used relations representative of typical and low-end dispersivities.

Note: Based on Gelhar's work, use of variable dispersivity values should yield a better estimate of concentration at each distance downgradient of the source. However, when using field data to calibrate the model and estimate rate coefficients, be aware that the Domenico model assumes constant dispersivity values. The user must choose between using a variable dispersivity that is likely to be more physically accurate at each point or a fixed dispersivity value that makes each point mathematically consistent with each other. In general, if the user would like the best estimate of concentration at each point in a BIOCHLOR simulation, use a variable dispersivity. If the user would like accurate mass balances between each point, use a fixed dispersivity. Fixed dispersivity values should be used for two-zone simulations.

BIOCHLOR is programmed with some commonly used relations based on x (distance from the source in ft) that are representative of typical and low-end dispersivities. The user also has the option to enter fixed diffusivity values.

- Longitudinal Dispersivity

The user is given three options:

> ***Option 1*** *(the default option)* allows the user to specify a fixed value for alpha x. One commonly used relation is to assume that alpha x is 10% of the estimated plume length.
>
> ***Option 2*** assumes that alpha x = 0.1* x
>
> ***Option 3*** calculates the longitudinal dispersivity using the following correlation:

$$\text{Alpha x} = 3.28 \cdot 0.82 \cdot \left[\log_{10}\left(\frac{x}{3.28}\right)\right]^{2.446}$$ (Xu and Eckstein, 1995; Al-Suwaiyan, 1996)

- **Transverse Dispersivity**

The user may choose a ratio of alpha y : alpha x. One commonly used ratio is:

> Alpha y: alpha x = 0.10 *(Based on high reliability points from* Gelhar et al., 1992)

- **Vertical Dispersivity**

The user may choose a ratio of alpha z : alpha x. One commonly used ratio is:

> Alpha z: alpha x = 0.05 *(ASTM, 1995)*

Alternatively, alpha z :alpha x can be set to a very low number (e.g., E-99) to yield a conservative estimate of vertical dispersion. This is the default value used in BIOCHLOR.

Other commonly used relations include:

> Alpha x = 0.1 Lp *(Pickens and Grisak, 1981)*

Alpha y = 0.33 alpha x	*(ASTM, 1995) (EPA, 1986)*
Alpha z = 0.05 alpha x	*(ASTM, 1995)*
Alpha z = 0.025 alpha x to 0.1 alpha x	*(U.S. EPA, 1986)*

The BIOCHLOR input screen includes Excel formulas to estimate dispersivities from scale. BIOCHLOR uses the modified Xu and Eckstein (1995) algorithm for estimating longitudinal dispersivities because 1) it provides lower range estimates of dispersivity, especially for large values of x and 2) it was developed after weighing the reliability of the various field data compiled by Gelhar *et al.* (1992) (see Figure A.3). BIOCHLOR also employs low-end estimates for transverse and vertical dispersivity estimates (0.10 * alpha x and 0, respectively) because these relations better fit high reliability field data reported by Gelhar *et al.* (see Figure A.4), and Gelhar *et al.* recommend use of values in the lower range of the observed data. The user can also enter a fixed longitudinal dispersivity value in the "Change Alpha x Calc." dialog box on the input screen.

Note that the Domenico model and BIOCHLOR are not formulated to simulate the effects of chemical diffusion. Therefore, contaminant transport through very slow hydrogeologic regimes (e.g., clays and slurry walls) should probably not be modeled using BIOCHLOR unless the effects of chemical diffusion are proven to be insignificant.

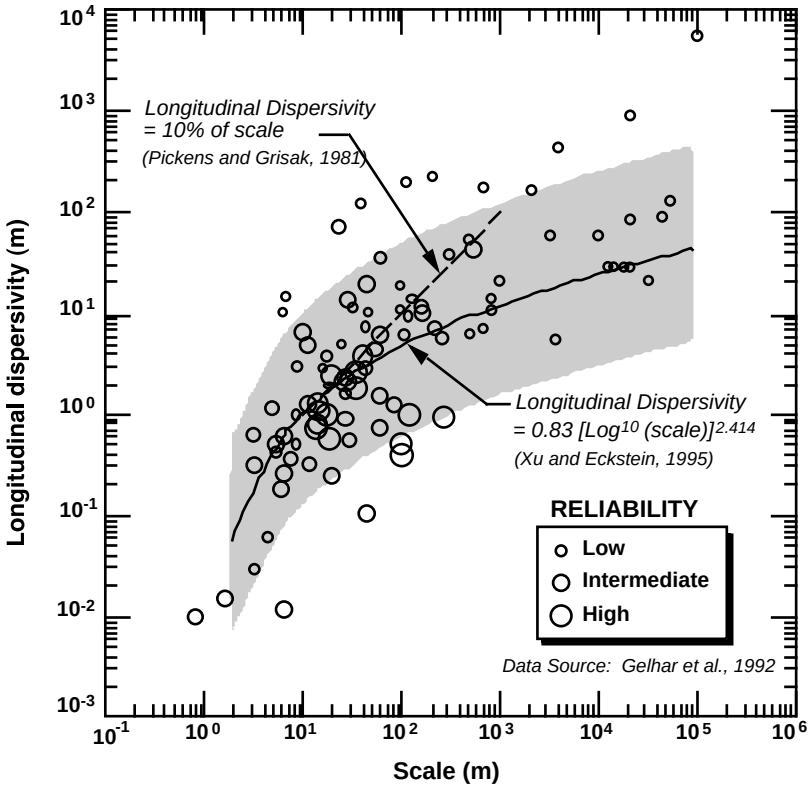


Figure A.3. Longitudinal dispersivity vs. scale data reported by Gelhar et al. (1992). Data includes Gelhar's reanalysis of several dispersivity studies. Size of circle represents general reliability of dispersivity estimates. Location of 10% of scale linear relation plotted as dashed line (Pickens and Grisak, 1981). Xu and Eckstein's regression shown as solid line. Shaded area defines ±1 order of magnitude from the Xu and Eckstein regression line and represents general range of acceptable values for dispersivity estimates.

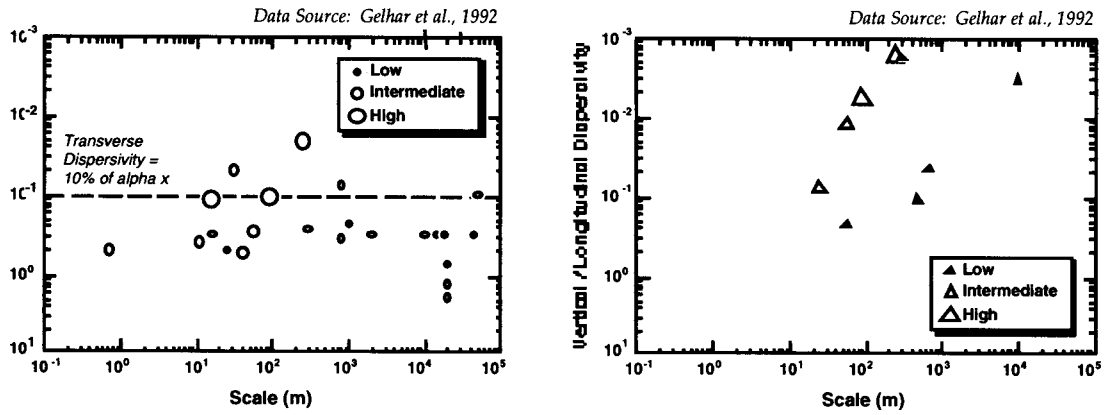


Figure A.4. Ratio of transverse dispersivity and vertical dispersivity to longitudinal dispersivity data vs. scale reported by Gelhar et al. (1992). Data includes Gelhar's reanalysis of several dispersivity studies. Size of symbol represents general reliability of dispersivity estimates. Location of transverse dispersivity relation used in BIOCHLOR is plotted as dashed line.

Appendix A.5

Pump and Treat Comparison

A useful way to estimate the clean-up time for a contaminated aquifer is to consider the number of pore volumes that must be pumped from the contaminated zone to achieve clean-up goals. A pump and treat module was added to the BIOCHLOR array output page to permit users to test the feasibility of pump and treat systems and to compare pump and treat clean-up times with natural attenuation predictions.

The user is provided with the volume of ground water in the plume (i.e., a pore volume). One pore volume is only a small fraction of the volume of ground water requiring treatment because dense non-aqueous phase liquids (DNAPLs), such as solvents, and sorbed constituents act as continuing sources of ground-water contamination. The number of pore volumes required for clean-up (i.e., the number of times the contaminated region must be flushed) is a function of many different factors including: the clean-up standard, the initial chemical concentration, the degree of mixing of clean and contaminated ground water, geologic heterogeneities, the presence and quantity of DNAPL, and sorbed constituents (NRC, 1994).

In the pump and treat module, the user enters the system pumping rate, and the number of pore volumes treated/ removed in one year is calculated by the program. This value provides the user with an indication of the feasibility of the pump and treat system. If the extraction rate is less than one pore volume per year, the attainment of clean-up criteria will likely take decades, even under the most favorable conditions (NRC, 1994).

Another cell asks the user to input the number of pore volumes that must be removed in order to clean up the aquifer. Using this value and the pumping rate, the time to clean up the contaminated aquifer can be estimated. The number of pore volumes required to remediate the aquifer is a site-specific and technology-specific value. The document, "Guidance on Remedial Actions for Contaminated Ground Water at Superfund Sites"(U.S. EPA, 1988), describes two methods for estimating ground-water clean-up times based on the number of pore volumes: the batch flushing model and the continuous flushing model. Neither of these methods account for DNAPL and, therefore, underestimate clean-up times. A third method accounting for DNAPL is reported in Newell *et al.* (1994) and Wiedemeier *et al.* (1999).

Appendix A.6

BIOCHLOR Example

Example : Cape Canaveral Air Station, Fire Training Area, Florida

Problem: Determine the concentration of TCE discharging into the canal in 1998, given data collected in 1997.

Given:

- Input Data
- Fig. A.5 Source Map
- BIOCHLOR Modeling Summary
- Fig. A.6 BIOCHLOR Input Data

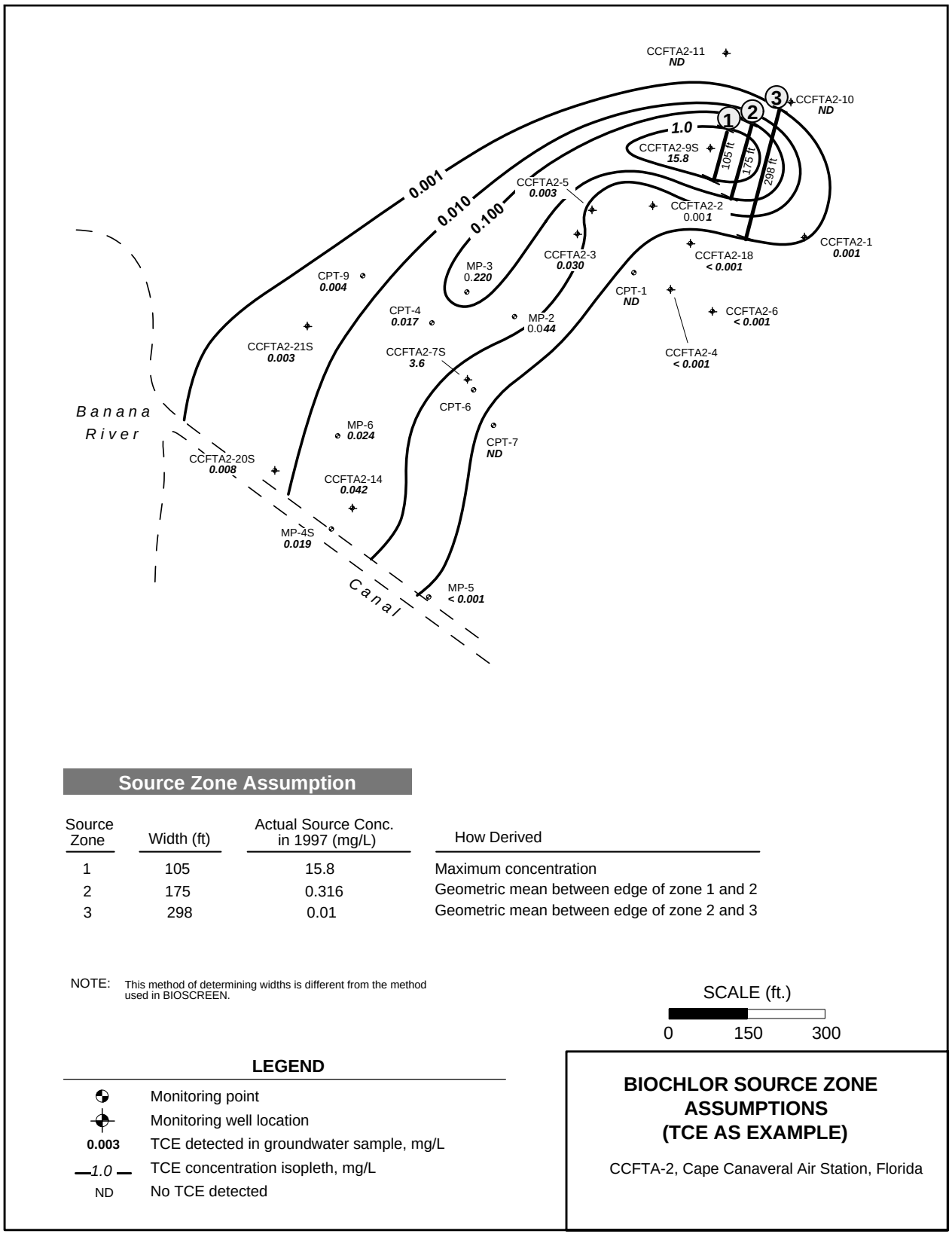
Results:

- Fig. A.7 BIOCHLOR Centerline Output
- Fig. A.8 BIOCHLOR TCE Centerline Output
- Fig. A.9 BIOCHLOR TCE Array Output

BIOCHLOR Example

Cape Canaveral Air Station, Florida

DATA TYPE	Parameter	Value	Source of Data
Hydrogeology	• Hydraulic Conductivity: • Hydraulic Gradient: • Effective porosity:	1.8×10^{-2} (cm/sec) 0.0012 (ft/ft) 0.2	• Slug-tests results • Static water level measurements • Estimated
Dispersion	• Longitudinal Dispersivity: • Transverse Dispersivity: • Vertical Dispersivity:	40 4 0 (ft)	• Intermediate value for 800-1200 ft. plume (from Gelhar et al. (1992)) • 0.1 x long. dispersivity • Assume vertical dispersivity is zero since depth of source is approx. depth of aquifer
Adsorption	• Individual Retardation Factors Common Retardation Factor • Aquifer Matrix Bulk Density • foc: • Koc:	PCE:7.1 TCE: 2.9 c-DCE: 2.8 VC: 1.4 ETH: 5.3 2.9 1.6 (kg/L) 0.184% PCE: 426 (L/kg) TCE: 130 (L/kg) c-DCE: 125 (L/kg) VC: 29.6 (L/kg) ETH: 302 (L/kg)	• Calculated from $R=1+K_{oc} \bullet f_{oc} \bullet \rho_b/n$ • Median value • Estimated • Lab analysis • Literature correlation using solubilities at 20 °C
Biotransformation	Biotransformation Rate Coefficients, (1/yr) PCE----> TCE TCE---->c-DCE c-DCE--->VC VC-----> ETH	 2.0 1.0 0.7 0.4	• Based on calibration to field data using a simulation time of 32 years (field data collected in 1997). Started with literature values and then adjusted model to fit field data
General	• Modeled Area Length: • Modeled Area Width: • Simulation Time:	1085 (ft) 700 (ft) 33 (yrs)	• Based on area of affected ground-water plume • From 1965 (first release) to 1998
Source Data	• Source Thickness: • Source Widths (ft) • Source Concentrations (mg/L) PCE TCE c-DCE VC ETH	56(ft) Area 1: 105; Area 2: 175; Area 3: 298 Area 1 / Area 2 / Area 3 0.056 / 0.007 / 0.001 15.8 / 0.316 / 0.01 98.5 / 1.0 / 0.01 3.080 / 0.089 / 0.009 0.030 / 0.013 / 0.003	• Based on geologic logs and monitoring data (see figure A.5 for TCE Example) • Modeled source area as variable source • Source concentrations are aqueous concentrations
Actual Data	Distance From Source (ft): PCE Conc. (mg/L): TCE Conc. (mg/L) c-DCE (mg/L) VC (mg/L) ETH (mg/L)	560 / 650 / 930 / 1085 <0.001 / ND / <0.001 / <0.001 0.220 / 0.0165 / 0.0243 / 0.019 3.48 / 0.776 / 1.200 / 0.556 3.080 / 0.797 / 2.520 / 5.024 0.188 / ND / 0.107 0.150	• Based on 1997 observed concentrations at site near centerline of plume
OUTPUT	Centerline Concentration:	See Figures A.7, A.8	
	Array Concentration:	See Figure A.9	



Source Zone Assumption

Source Zone	Width (ft)	Actual Source Conc. in 1997 (mg/L)	How Derived
1	105	15.8	Maximum concentration
2	175	0.316	Geometric mean between edge of zone 1 and 2
3	298	0.01	Geometric mean between edge of zone 2 and 3

NOTE: This method of determining widths is different from the method used in BIOSCREEN.

SCALE (ft.)

0 150 300

LEGEND

- Monitoring point
- Monitoring well location
- **0.003** TCE detected in groundwater sample, mg/L
- *1.0* TCE concentration isopleth, mg/L
- ND No TCE detected

BIOCHLOR SOURCE ZONE ASSUMPTIONS (TCE AS EXAMPLE)

CCFTA-2, Cape Canaveral Air Station, Florida

Figure A.5. BIOCHLOR source zone assumptions (TCE as example).

BIOCHLOR Modeling Summary,

Cape Canaveral Air Station, Florida

Entering Input

- BIOCHLOR was used to reproduce the movement of the plume from 1965 (the best guess for when the release occurred) to 1998.
- The hydraulic conductivity, hydraulic gradient, and the effective porosity were entered and the “C” button was pressed to generate the seepage velocity.
- For longitudinal dispersivity, a fixed dispersivity of 40 ft (Option 1) was chosen. The ratio of lateral dispersivity to longitudinal dispersivity was set to 0.1 and the vertical dispersivity was set to 0. This last value was chosen because the depth of the source area is similar to the depth of the saturated zone.
- To determine the retardation factors, the aquifer matrix bulk density, the partition coefficients at 20^{o}C, and the fraction of organic carbon were input into the gray cells and the “C” button was pushed to yield the retardation factors. BIOCHLOR uses one retardation factor, not individual retardation factors for each constituent. The default value for the common retardation factor is the median retardation factor, but the user can over-ride this value. In cases where the retardation factor varies significantly among the constituents, it is advisable to do a sensitivity analysis to determine how the choice of the common R affects the model predictions. For this simulation, the median value of 2.85 was chosen.
- For modeling biotransformation, the user has the choice of modeling the plume in one or two zones. Modeling in two zones permits the use of a different set of rate coefficients in each zone, but requires that the plumes be at steady state (as established from field data). In this example, we will model the plume as one anaerobic zone using one set of rate coefficients. (Field dissolved oxygen, ORP, and geochemical data were used to establish anaerobic conditions.) Because field-scale rate coefficients and rate data from microcosms were unavailable, rate coefficients previously obtained by calibrating the model to 1997 field data were used. Here, the rate coefficients were entered into the white cells.
- In the General Section, the model area length, width, and simulation time must be entered. The model area length is the distance from the source to the receptor (the canal, in this case study). A width of 700 ft is chosen to be significantly larger than the plume width to capture all of the mass discharging into the canal. A simulation time of 33 years was chosen because the simulation is being conducted for 1998, and the solvents were released starting in 1965.
- Because we are interested in centerline predictions and the mass flux into the canal, the source area will be modeled as a spatially-variable source. By pressing the “Source Options” button and selecting “Spatially-Variable Source”, a dialog box pops up that allows for the input of source area concentration and width data. To obtain the most conservative centerline predictions, the maximum concentration in the source area were used for zone 1. The other two concentrations were obtained by taking the geometric means between adjacent isopleths (see Figure A.5). Once these data are entered and “OK” is pressed, the data are transferred to the input page and you will see the layout shown in Figure A.6. Note that any subsequent changes to the source area concentrations can be done directly on the input page without going through the dialog box. Lastly, the thickness of the source area was determined by entering the deepest depth where chlorinated solvents were detected in the aqueous phase.
- Finally, there is an input area for field data. In this example, the 1997 field data were used (previously) to determine the rate constants provided. If one does not have field-scale rate constants or rate data from microcosm studies, these values become important for calibrating the model.

Viewing Output

- There are two choices for viewing the output. Centerline predictions are shown for all five species in Figure A.6 and for TCE in Figure A.8. Figure A.7 shows the centerline predictions for each chlorinated solvent and a no degradation curve for all of the chlorinated solvents added together as well as field data. From this screen, the user can view the centerline predictions of each constituent individually or go to the array screen. Figure A.8 shows the centerline prediction for TCE, with and without biotransformation. However, any of the constituents can be viewed by pressing the buttons to the right of the graph. Here we can see that the TCE concentration discharging into the canal (at 1085 ft) is 0.003 mg/L.

- From this screen or from the input screen the array page can be selected. The array output for this problem is displayed in Figure A.9. This three-dimensional figure shows the longitudinal and lateral extent of contamination. Again, the user can select the constituent to be viewed and the no degradation or biotransformation prediction. Note that the scale on the array automatically changes depending on the magnitude of the concentrations. These array values are maximum values because the array is evaluated at z=0.

Other information that is presented on the output screen includes the mass removed, the percent biotransformed, and the mass flux. The TCE mass flux discharging to the canal is approximately 83 mg/day.

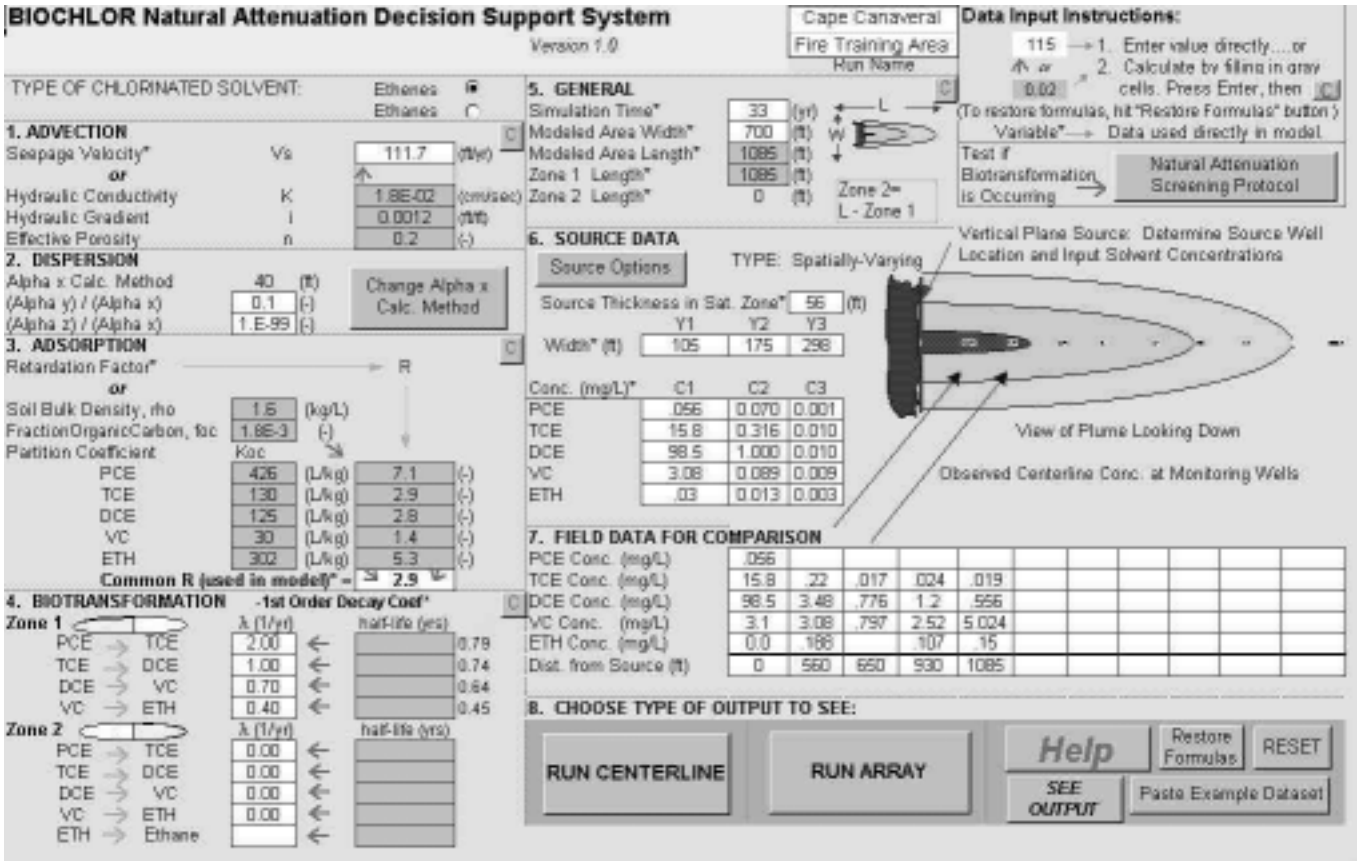


Figure A.6. BIOCHLOR input screen. Cape Canaveral Air Force Base, Florida.

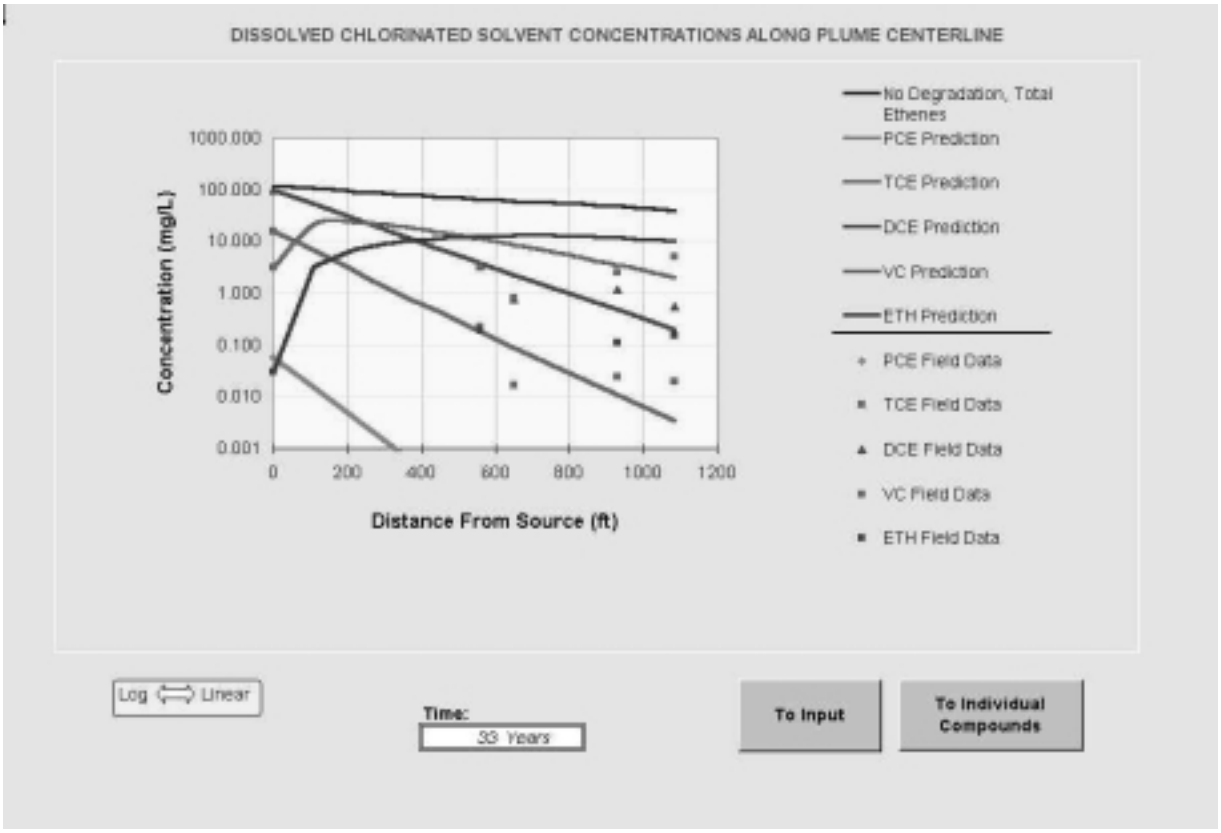


Figure A.7. Centerline output. Cape Canaveral Air Force Base, Florida.

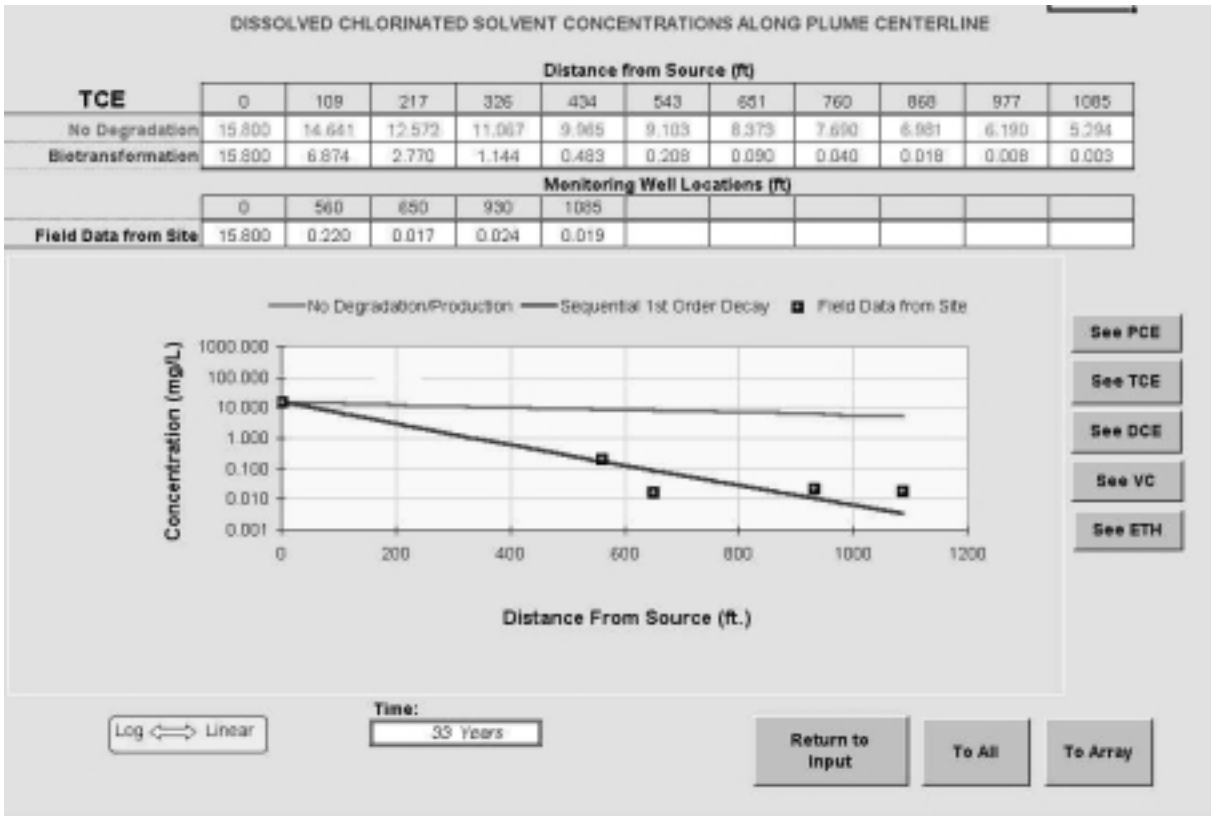


Figure A.8. Individual centerline output for TCE, Cape Canaveral Air Station, Florida.

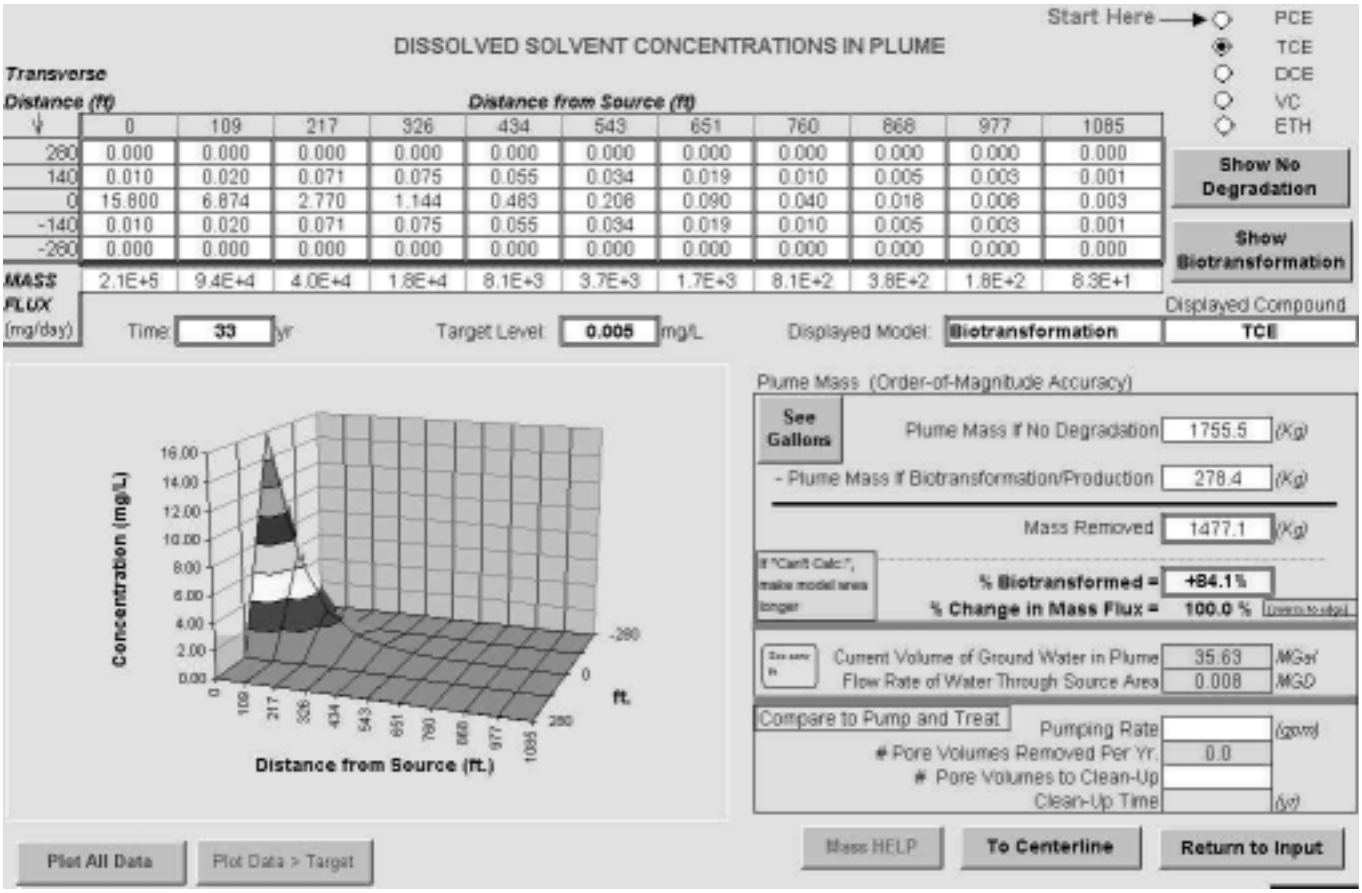


Figure A.9. Array concentration output for TCE. Cape Canaveral Air Station, Florida.

Sensitivity Analysis Examples

Sensitivity analyses are recommended when literature values are used or if there is uncertainty in an input parameter. To illustrate the response of the BIOCHLOR model to changes in the input parameters, a sensitivity analysis was conducted for the first order decay coefficients and also for the common retardation factor.

In the first sensitivity analysis example, the case study (baseline) problem was run with the same input parameters except that the first order decay coefficients were multiplied by 2. Similarly, another simulation was conducted whereby the rate coefficients were 0.1 times those used in the baseline example. The centerline concentrations of PCE, TCE and the daughter products 1085 ft downgradient from the source are shown in Table A.4 for each simulation. In this instance, the simulated concentrations of PCE and its daughter products increase substantially when the rate coefficient is decreased by a factor of ten and doubling the rate coefficient decreases the chlorinated solvent concentrations at the canal location. In this example, the chlorinated ethene concentrations are very sensitive to the magnitude of the rate coefficient.

TableA.4. Sensitivity Analysis Results - Rate Coefficients

Constituent	***Concentrations (mg/L)***		
	2X Baseline	**Baseline ***	**0.1X Baseline**
PCE	0.000	0.000	0.006
TCE	0.000	0.003	2.254
DCE	0.003	0.202	19.443
VC	0.137	2.039	8.819

baseline $\lambda_{PCE \rightarrow TCE}$=2.00 yr^{-1}, $\lambda_{TCE \rightarrow DCE}$ =1.00 yr^{-1}, $\lambda_{DCE \rightarrow VC}$ =0.70 yr^{-1}, $\lambda_{VC \rightarrow ETH}$ =0.40 yr^{-1}

In contrast, changes in the retardation factor have nominal effects on the dissolved chlorinated solvent concentrations as shown in Table A.5. In this sample case, when the retardation factor is decreased from the baseline value of 2.9, chlorinated solvent concentrations increase slightly. Also, with an increase in the retardation factor chlorinated solvent concentrations at the canal location decrease by a small amount. These small variations in the concentrations due to the changes in the retardation factor can probably be attributed to the plume being near steady-state in this example.

Table A.5. Sensitivity Analysis Results - Retardation Factor

Constituent	***Concentrations (mg/L)***		
	R=1.4	**R=2.8 (Baseline)**	**R=4.7**
PCE	0.000	0.000	0.000
TCE	0.003	0.003	0.003
DCE	0.204	0.202	0.112
VC	2.161	2.039	0.798

In this example, the BIOCHLOR model is more sensitive to changes in the first-order decay coefficient and less sensitive to changes in the retardation factor. However, the results of these sensitivity analyses are site-specific and do not apply to all sites.