

REMChlor

Remediation Evaluation Model for Chlorinated Solvents

User's Manual Version 1.0

by

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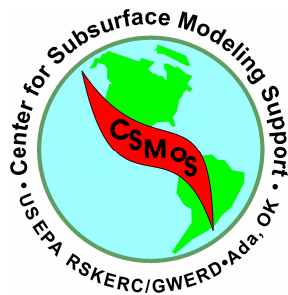
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Overview

Abstract

A new analytical solution has been developed for simulating the transient effects of groundwater source and plume remediation. This development was performed as part of a Strategic Environmental Research and Development Program (SERDP) research project, which was a joint effort between the US EPA, Clemson University, Purdue University, the University of Florida, and the Air Force Institute of Technology, focused on defining the benefits of partial DNAPL source remediation.

The analytical model is called **REMChlor** (for **R**emediation **E**valuation **M**odel for **C**hlorinated Solvents). In the new analytical method, the contaminant source model is based on a power function relationship between source mass and source discharge, and it can consider partial source remediation at any time after the initial release. The source model serves as a time-dependent mass flux boundary condition to the analytical plume model, where flow is assumed to be one-dimensional. The plume model simulates first order sequential decay and production of several species, and the decay rates and parent/daughter yield coefficients are variable functions of time and distance. This approach allows for flexible simulation of enhanced plume degradation that may be temporary in time, limited in space, and which may have different effects on different contaminant species in the decay chain. Cancer risks posed by carcinogenic species in the plume are calculated assuming that the contaminated water is used in a house for drinking, bathing, and other household uses.

The Center for Subsurface Modeling Support (CSMoS) at EPA has developed a Graphical User Interface (GUI), for **REMChlor** that will allow the user to quickly and easily evaluate the balance of DNAPL source remediation, plume remediation, and natural attenuation. The GUI consists of a user-friendly, visually intuitive model parameter data entry screen, and a variety of quick and powerful ways of displaying the resulting model output.

The primary objective of the **REMChlor** GUI is to simplify model data input, and viewing/interpreting model data output. The GUI is written in Visual Basic. It will compile the model input file, run the input file through the FORTRAN model code, and provide a seamless way of working with the resulting output data files.

This version of **REMChlor** provides a suite of powerful tools for building and interpreting models. The manual will be periodically updated to include new functions and related theoretical background.

DISCLAIMER OF LIABILITY

With respect to **REMChlor** software and documentation, neither the United States Government, Clemson University, nor any of their employees, assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed. Furthermore, software and documentation are supplied "as-is" without guarantee or warranty, expressed or implied, including without limitation, any warranty of merchantability or fitness for a specific purpose.

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REMChlor Software Installation and Computer Requirements

1. To install the software, run the file 'REMCHLORsetup.exe'. The software will guide the user through the installation process. Upon first running this version of REMChlor from the desktop icon, the user will be asked to run it again. This serves to initialize the application after which REMChlor will run properly in Microsoft Windows®.
2. REMChlor v 1.0 requires a standard PC running Microsoft Windows 98 or greater and Microsoft.NET. The Microsoft.Net framework that is required comes with the setup.exe and will be loaded with the application. Minimum requirements for the .Net framework are a Pentium 90 MHz or faster processor and 32 MB of RAM or higher (96 MB or higher recommended).

Analytical Mathematical Model

Background

Groundwater has been contaminated with chlorinated solvents (chlorinated volatile organic compounds, CVOCs) at thousands of sites in industrialized nations. Many of these sites contain dense nonaqueous phase liquids (DNAPLs) that serve as a concentrated source of groundwater contamination, and most dissolved plumes of CVOCs can be traced back to concentrated source zones. The CVOCs typically are believed to be carcinogens, and they have low maximum contaminant levels (MCLs) in drinking water. Considering that source concentrations can be four or five orders of magnitude greater than MCLs, restoration of source zones to pristine conditions seems unlikely; however, reduction of CVOC plumes is a realistic goal, that can be achieved through various combinations of source and plume remediation.

Much recent research has focused on technology development for both source and plume remediation. Several in-situ methods (soil vapor extraction, air sparging, steam flooding, six-phase electrical heating, thermal conduction heating, chemical oxidation, and surfactant and cosolvent flooding) are currently available for removing or destroying chlorinated solvent mass contained in the source zone (Reddi, 1996; Brusseau et al., 1999; Kaluarachchi, 2001; USEPA, 2004; Mayer and Hassanizadeh, 2005). Controlled experiments have demonstrated DNAPL removal in the range of 60 to >90% (USEPA, 2004). Source containment methods (slurry walls, sealable joint sheet-pile walls, clay caps), can also be used to remove or reduce the contaminant loading to the plume.

Destruction of CVOCs in dissolved plumes can occur under natural conditions by biodegradation processes including reductive dechlorination, aerobic oxidation, anaerobic oxidation, and aerobic co-metabolism (Weidemeier et al., 1999; NRC 2000; Alvarez and Illman, 2006). It is now fairly common to engineer in-situ biodegradation systems for enhancing one or more of these processes in order to allow the plume to attenuate in a shorter distance, or to reduce plume concentrations in locations that are detached from the source. These enhancements usually involve addition of an electron donor (hydrogen, lactate, molasses or a hydrogen releasing compound) for enhancing anaerobic processes, or an electron acceptor (oxygen, air, H₂O₂, or an oxygen releasing compound) for enhancing aerobic processes (Chapelle et al., 2003; Alvarez and Illman, 2006). In other cases, reactive barriers or basic hydraulic control through pump-and-treat are used to manage the dissolved plume.

These source and plume remediation efforts are expensive. Source remediation can cost anywhere from several hundred thousand dollars to tens of millions of dollars (McDade et al., 2005), and it is rarely (if ever) possible to remove all of the contaminant. The benefit of these source remediation efforts is that by removing source mass, they tend to reduce the mass discharge to the plume (Rao et al., 2001; Rao and Jawitz, 2003; Falta et al., 2005a; Fure et al., 2005; Jawitz et al. 2005). The reduced plume

loading following source remediation may or may not be sufficient to allow natural attenuation processes to keep the plume within acceptable limits (Falta et al., 2005a,b).

Costs for plume remediation are usually considered to be smaller than those for source remediation because of the lower capital costs. At sites where the source is nearly depleted by dissolution or other processes, plume remediation would tend to be the most cost effective strategy for site management. However, if substantial source mass is present, in the absence of source remediation, the plume remediation systems must be operated for a long period of time. In this case, the operating costs (in terms of present worth) can be comparable to the costs of source remediation. A reasonable strategy for many sites would be some combination of source and plume remediation. Selection of the optimal remedy for a site, in terms of the degree of remediation must consider the inherent coupling of the source remediation to the plume remediation.

Experience with natural attenuation as a remedy for plume management has shown that mathematical models can play an important role in the remedy selection process (Weidemeier et al., 1999; NRC, 2000; Alvarez and Illman, 2006). In many cases, screening level simulations performed with analytical models such as BIOCHLOR (Aziz et al., 2000) or BIOSCREEN (Newell et al., 1996) are effective for demonstrating the applicability of natural attenuation. A recent study of 45 CVOC sites found that mathematical models were used at 60 percent of the sites, and that BIOCHLOR was the most frequently used model (McGuire et al., 2004). These types of analytical models are also commonly used to estimate exposures for risk assessment.

In this section, the analytical screening level model that couples source and plume remediation is presented. The contaminant source can be depleted naturally by processes of dissolution and first order decay, and the effects of a delayed removal or destruction of part or all of the source is considered. The contaminant source is analytically coupled to a plume model that considers 1-D advection, retardation, and 3-D dispersion with first order decay of parent compounds into daughter products. The plume model considers all of the contaminant reaction rates and yield coefficients to be independent functions of distance from the source and time since the contaminant release. This approach allows for flexible simulation of enhanced plume degradation that may be temporary in time, limited in space, and which may have different effects on different contaminant species in the decay chain.

Since many contaminants of concern are carcinogenic, cancer risks are calculated for each species in the plume, assuming that contaminated well water is piped into a house, and used for drinking, bathing, and other household uses. The cancer risk model thus allows for an assessment of the relative reductions in risk that various remediation activities would have.

DNAPL Source Model with Remediation

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

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

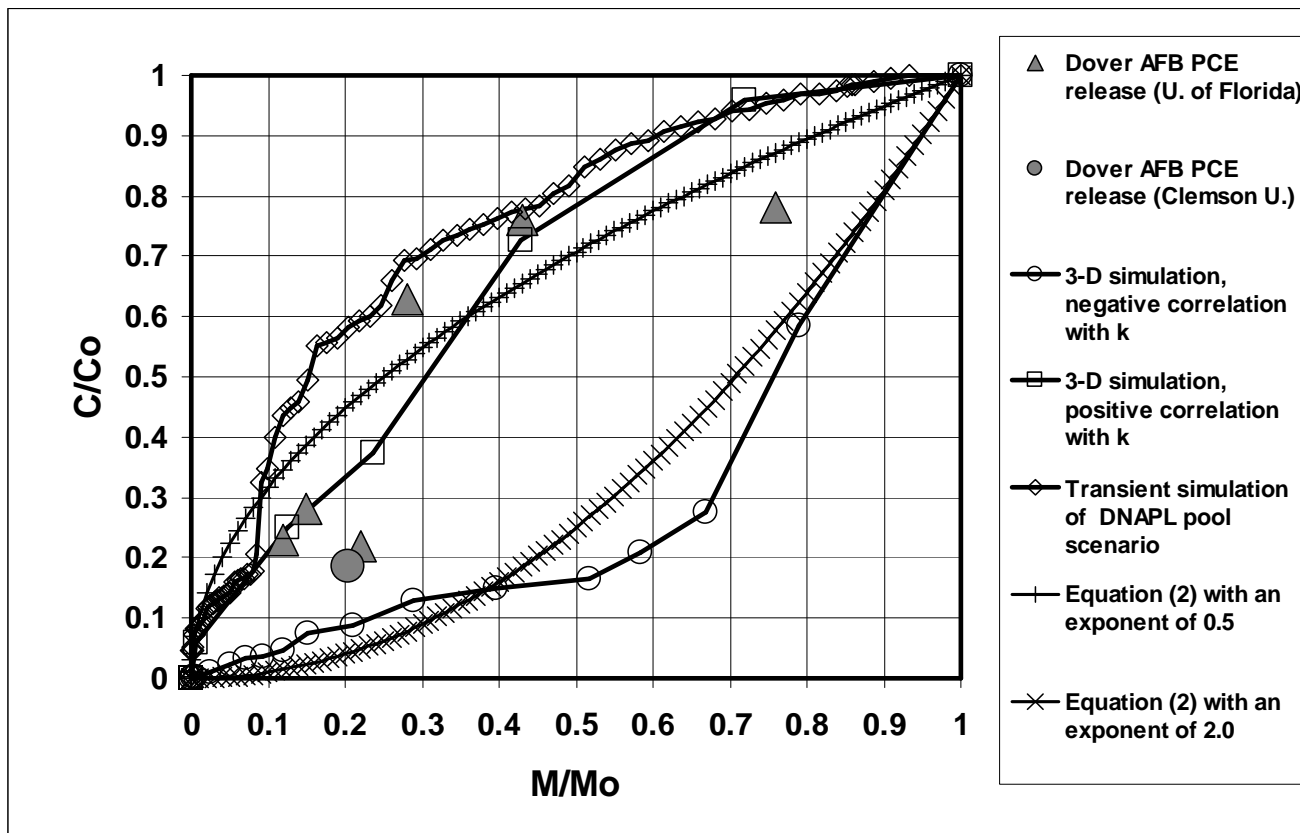


Figure 1. Source zone dissolved concentrations as a function of source zone DNAPL mass (from Falta et al., 2005a).

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

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

removed. Although the individual extraction ports show somewhat variable responses over time, the integrated average of these produces a source mass/source discharge relationship that is fairly close to 1:1 (Fure et al., 2006).

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

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

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

The contaminant discharge from a source zone is the product of the flowrate of water passing through the source zone, and the average concentration of contaminant in that water (Figure 2). Source discharge thus has units of mass per time, and it is the surface integral of the mass flux, which is a discharge divided by an area. If contaminant-free water flows through the source region at a rate of $Q(t)$, and if the mass in the source zone is also subject to some form of chemical or biological first order decay, then a mass balance on the source gives:

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

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

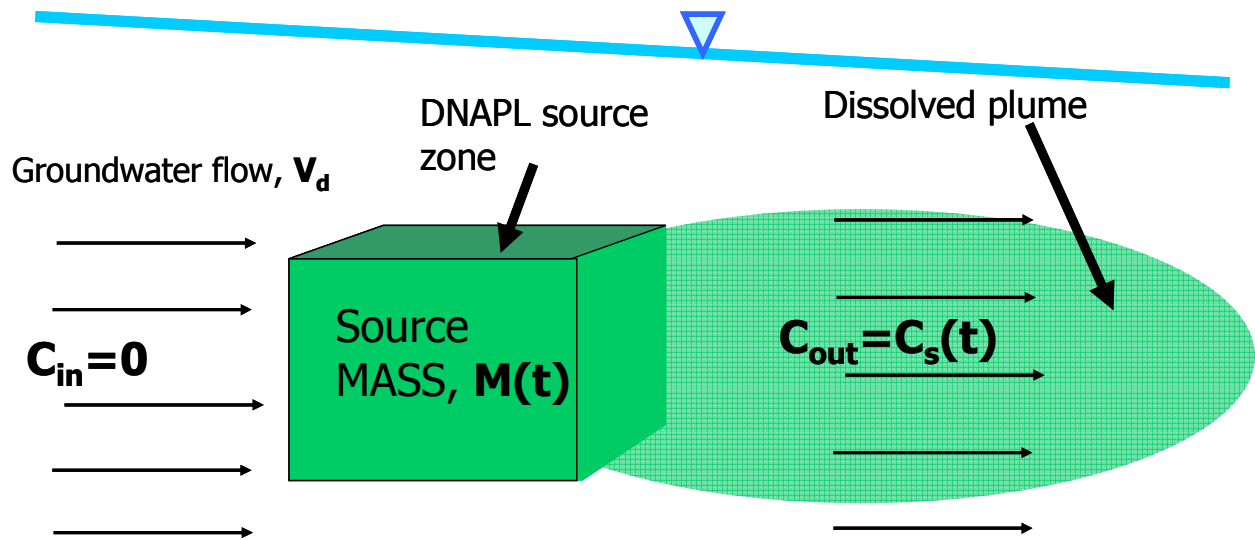


Figure 2. Conceptual model of source zone with time-dependent contaminant mass and discharge.

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

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

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

Rao and Jawitz (2003) used a streamtube modeling approach to study the variation of source discharge with source mass. They assumed a heterogeneous collection of streamtube velocities that were log-normally distributed, with a uniform NAPL distribution. They found that as the standard deviation of the velocity field became small, that the source discharge and source mass tended to be linearly related ($\Gamma \sim 1$). Parker and Park (2004) modeled a hypothetical DNAPL spill and dissolution in a three-dimensional, heterogeneous setting. They found that the best fit value of Γ was about 1.1 for the upper part of their simulation domain, and 0.4 in the lower part of the simulation domain. Figure 1 shows Equation (2) plotted with $\Gamma = 0.5$ and 2 for comparison.

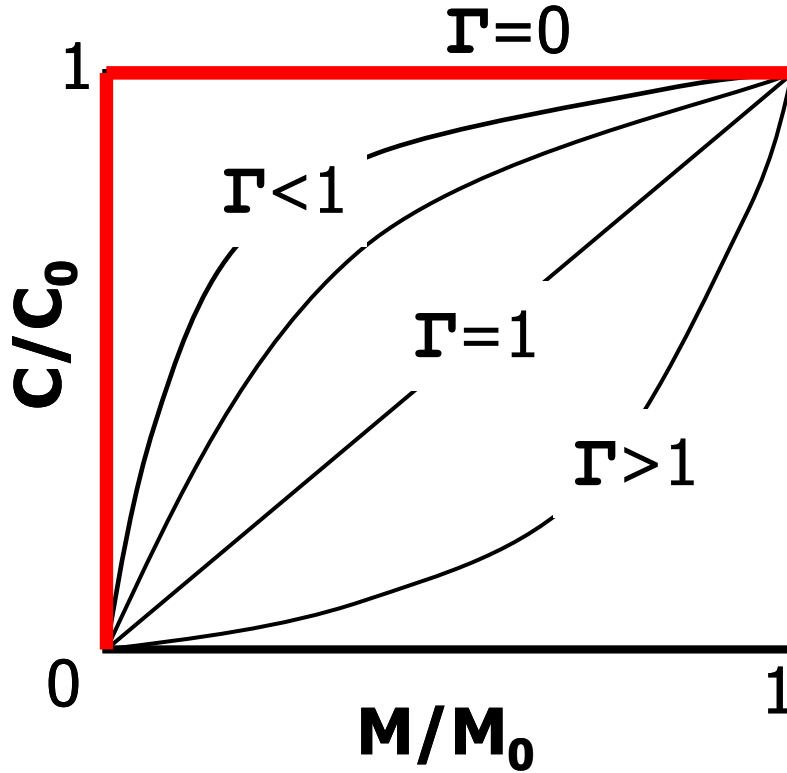


Figure 3. Power function representation of source mass/source discharge relationship (Equation 2).

If the water flow rate through the source zone in Equation (1) is assumed to be constant, the power function (Equation 2) can be substituted to get:

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

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

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

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

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

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

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

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

and

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

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

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

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

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

and the source completely disappears at a time of

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

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

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

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

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

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

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

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

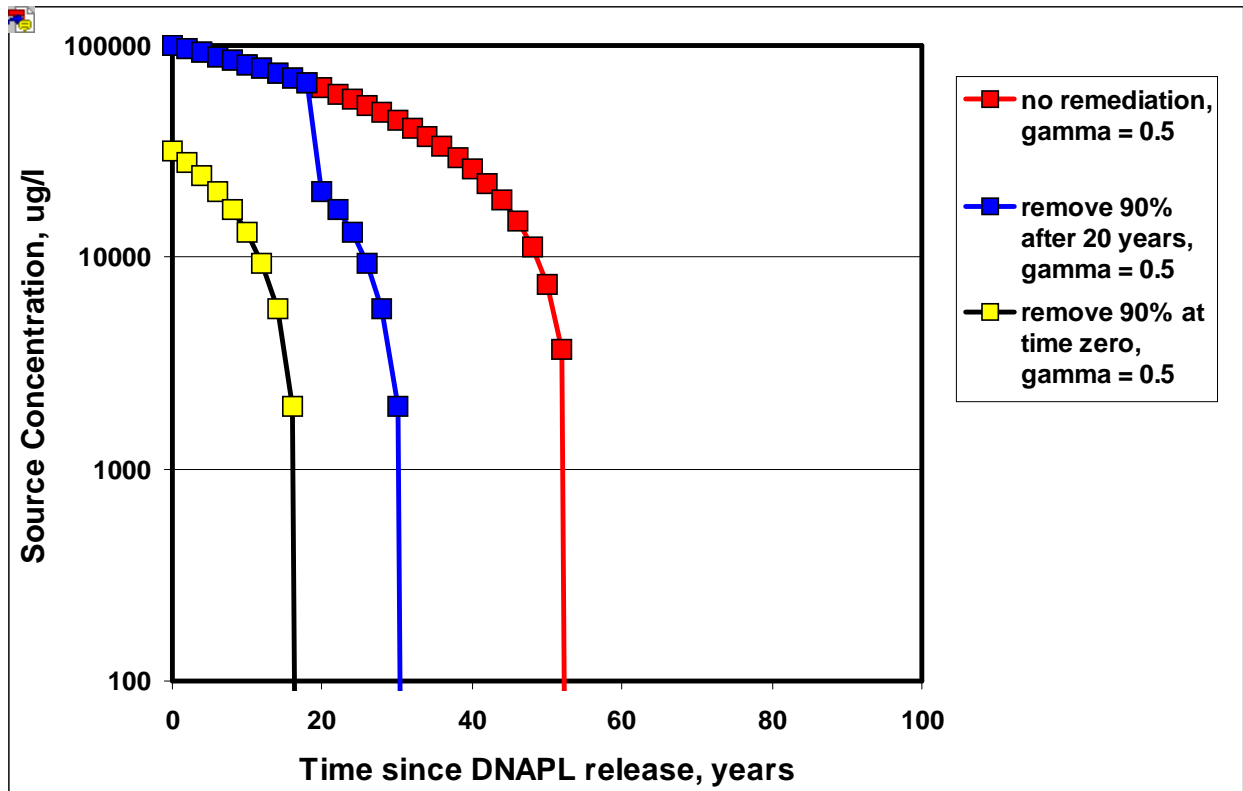


Figure 4. Source zone dissolved concentrations with and without source remediation for $\Gamma = 0.5$ (from Falta et al., 2005a)

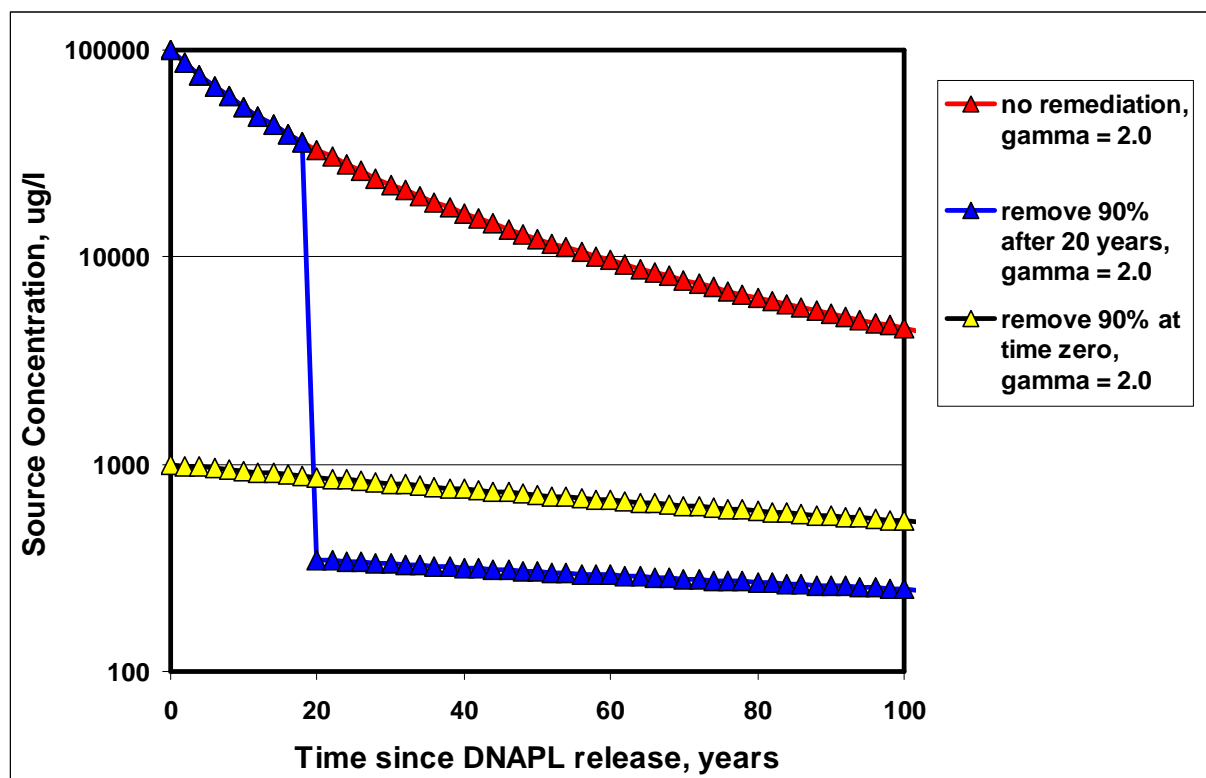


Figure 5. Source zone dissolved concentrations with and without source remediation for $\Gamma = 2.0$ (from Falta et al., 2005a)

Coupled Plume Model with Enhanced Biodegradation

Falta et al. (2005b) used Equations (5) and (11) to form a mass flux boundary condition used in an advection-dispersion equation with first order parent-daughter decay reactions. A significant limitation of that solution was that it required the solute decay rates in the plume to be constant in both space and time. There are many cases in which the decay rates of the compounds are spatially variable, or where they are manipulated in space and time through the addition of electron donors, electron acceptors, oxygen or nutrients.

The current analytical approach assumes a constant groundwater pore velocity of v in the x -direction, with longitudinal, transverse, and vertical dispersion. The solute can be retarded by adsorption, but the different solutes involved in coupled reactions must have the same retardation factor. These assumptions are similar to those used in previous natural attenuation plume models such as BIOCHLOR (Aziz et al., 2000; 2002), BIOSCREEN (Newell et al., 1996), LNAST (Huntley and Beckett, 2002), and the model by Falta et al. (2005b).

The BIOCHLOR model allows for two spatial zones to be defined in which the solute decay rates are different, but this is only valid if the solute concentrations in the upstream zone are at steady-state, which implies a constant source concentration in time. The solute decay rates in BIOCHLOR are constant

in time. The other analytical models assume that the reaction rates are constant in both space and time. The key difference in the present plume model and these previous models, is that the chemical reaction parameters (rates, yield coefficients) can now be arbitrary functions of both time and distance from the source.

The governing equation for the dissolved concentration of each contaminant species in the plume, C , is:

$$R \frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial x} + \alpha_x v \frac{\partial^2 C}{\partial x^2} + \alpha_y v \frac{\partial^2 C}{\partial y^2} + \alpha_z v \frac{\partial^2 C}{\partial z^2} + rxn(x, t) \quad (14)$$

where α_x , α_y , and α_z are the longitudinal, transverse, and vertical dispersivities, respectively; R is the retardation coefficient, and $rxn(x, t)$ represents the rate of generation (+) or destruction (-) of the species due to chemical or biological reactions that are spatially and temporally variable. This plume model is coupled with the source zone mass balance given by Equation (1), using the power function relationship for the C_s vs M relationship (Equation (2)). A specified flux boundary condition at $x=0$ ensures that the rate of discharge from the source zone is exactly equal to the rate at which contaminants enter the plume (see van Genuchten and Alves (1982)). The mass flux entering the plume is specified as:

$$\frac{Q(t)C_s(t)}{A} = \left[\phi v C(t) - \phi \alpha_x v \frac{\partial C(t)}{\partial x} \right]_{x=0} \quad (15)$$

where A is the area over which the contaminant flux enters the groundwater flow system, and ϕ is the porosity. Outside of this area, the mass flux is zero. For sources that are located below the water table, A would be the cross-sectional area of the source zone perpendicular to the groundwater flow. For sources located above the water table, A would be the cross-sectional area at the top of the water table perpendicular to flow that was required to accommodate the infiltration rate from the source. Falta et al. (2005b) solved Equations (9) and (10) analytically for the case of first order decay reactions with constant and uniform decay rates, using a Laplace transform method, combined with Domenico's (1987) approximation for transverse and vertical dispersion. Analytical solution of Equation (14) with variable plume reaction rates by this method would be much more difficult. Instead, a different approach is taken where the solute advection and reactions are decoupled from the longitudinal dispersion using a simple streamtube technique. Scale-dependent longitudinal dispersion is accounted for by considering a collection of streamtubes with a normally distributed pore velocity. Transverse and vertical dispersion are then simulated using Domenico's (1987) approximation.

The reactive plume model is based on a simple one-dimensional streamtube that is characterized by a constant pore velocity and solute retardation factor. Since there is only advection taking place in the streamtube, the flux boundary condition at the edge of the source zone simplifies to

$$C(t) \Big|_{x=0} = \frac{Q(t)C_s(t)}{\phi v A} \quad (16)$$

If the source is located below the water table, and $Q = \phi v A$, then the flux boundary condition is just the time-dependent source concentration,

$$C(t) \Big|_{x=0} = C_s(t) \quad (17)$$

where $C_s(t)$ could be calculated, for example, by Equations (5) and (11).

One-dimensional advective transport of a solute can be represented graphically on a distance-time plot (Figure 6). Here, the time axis corresponds to the time since the contaminant was first released to the groundwater system, while the distance axis is the distance downstream from the source.

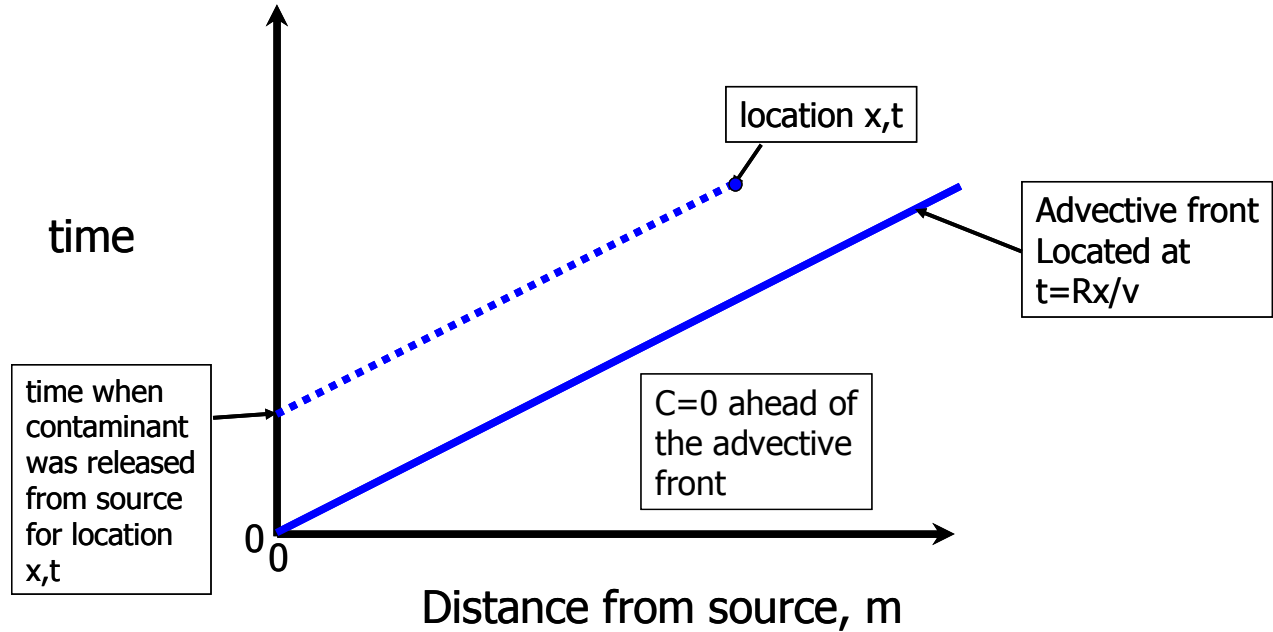


Figure 6. Distance-time plot for advective transport with a single set of plume reaction rates.

The advective front moves at a constant velocity of v/R , so that at any location, x , the front passes by at a time of $t=Rx/v$. At any time, the front is located at $x=vt/R$, and the solute concentration is always zero below this line (ahead of the front). In the absence of any plume degradation process, the concentration at any location behind the advective front can be determined from the time of solute release from the source, $t_{release}$. For a distance from the source, x , the travel time is $t_{travel}=Rx/v$. Therefore, if the total time is t , the parcel of water found at that location (x,t) was released from the source at a time of

$$t_{release} = t - Rx/v \quad (18)$$

and the concentration at that (x,t) point would be

$$C(x,t) = C(t_{release})|_{x=0} \quad (19)$$

Plume reactions can easily be included in this advective streamtube model. As a parcel of solute is translated downstream, it is not subject to any mixing processes, so it is conceptually equivalent to a batch reaction that starts at time $\tau=0$ with an initial condition of $C(t_{release})|_{x=0}$ and reacts for a period of time equal to the travel time to position x , $\tau=Rx/v$. As an example, if the solute reaction was first order decay in the aqueous phase with a decay rate coefficient of k , then the equivalent batch reaction is

$$R \frac{dC}{d\tau} = -k C \quad \text{with} \quad C|_{z=0} = C(t_{\text{release}})|_{x=0} \quad (20)$$

Then at location (x,t) behind the front, the solute concentration would be

$$C(x,t) = C(t - Rx/v)|_{x=0} \exp\left(\frac{-kx}{v}\right) \quad (21)$$

This result is exactly the same as the Laplace transform solution to Equations (14) and (15) with zero dispersion (Falta et al., 2005a). More complicated coupled reactions can be considered using this same method, but a fundamental limitation is that all of the reacting solutes must move at the same velocity in the groundwater, so they must be assumed to have a single retardation factor, R .

The analysis can be extended to the case of time and distance dependent reaction rates by dividing the time-distance domain into distinct zones (Figure 7). Here, nine zones have been chosen to approximately represent conditions downgradient from a contaminant source over the life of a plume. The first time zone after the spill, $t < t_1$, could represent a period following the contaminant release where no manipulation of the plume has yet been attempted; a period of natural attenuation. The second time zone after the spill, $t_1 < t < t_2$ could represent a temporary period of active plume remediation (enhanced attenuation). The final time zone, $t > t_2$, could be used to represent to long term conditions in the plume after manipulation of the plume ended (another period of natural attenuation).

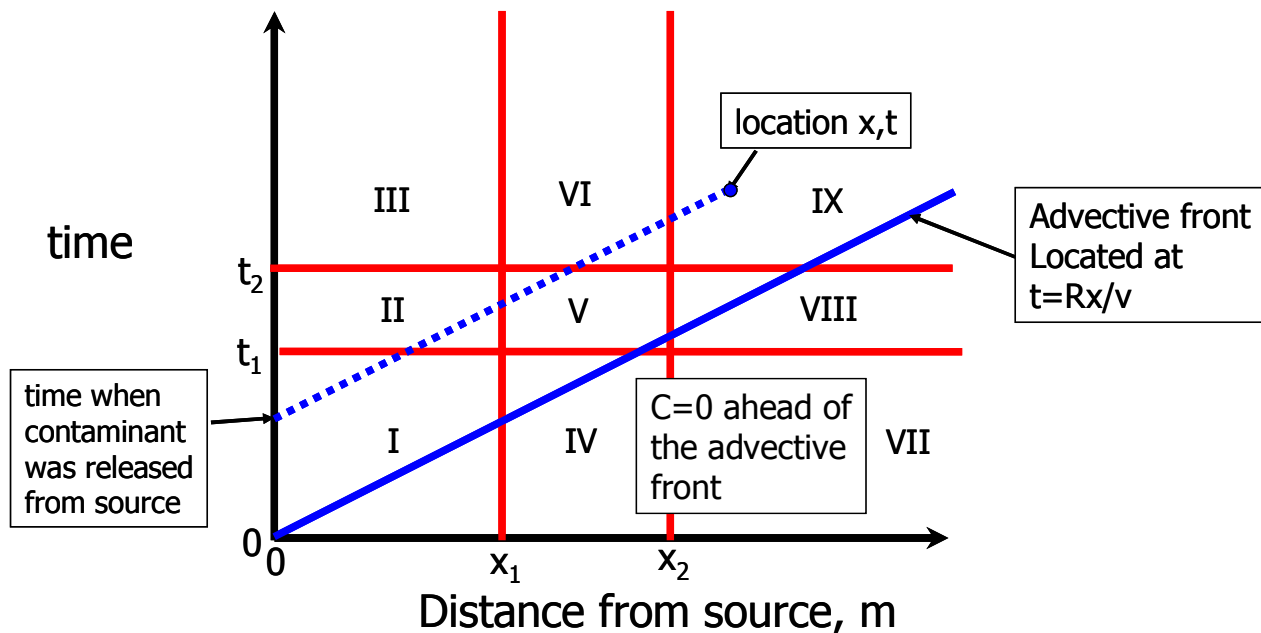


Figure 7. Distance-time plot for advective transport with multiple sets of plume reaction rates.

Distance from the source is similarly divided into zones so that near the source, for $x < x_1$, one set of natural or engineered biogeochemical conditions predominate, while downstream, at $x_1 < x < x_2$, another set of conditions are present. Beyond x_2 , conditions might again revert back to natural background conditions. These reaction zones are assumed to extend over the entire model domain in the lateral (y) and vertical (z) directions.

An example of how these different plume reaction zones might be used is shown in Figure 8. Here it is assumed that there was a release of tetrachloroethylene (PCE) in 1975, but plume remediation did not begin until 2005, with a planned duration of 20 years. In the absence of any significant electron donor supply, or other enhancements, natural conditions would prevail from 1975 to 2005. The plume remediation scheme could consist of the addition of electron donor in the first 400 m of the plume to increase the rate of reductive dechlorination of PCE and its daughter product, trichloroethylene (TCE). Because the daughter products cis-1,2-dichloroethylene (DCE) and vinyl chloride (VC) do not degrade as readily by reductive dechlorination, but they can degrade aerobically, a different reaction zone could be created from 400 to 700 m, where aerobic degradation was stimulated (Chapelle et al., 2003; Alvarez and Illman, 2006). Downgradient of this zone, conditions might revert back to their natural state.

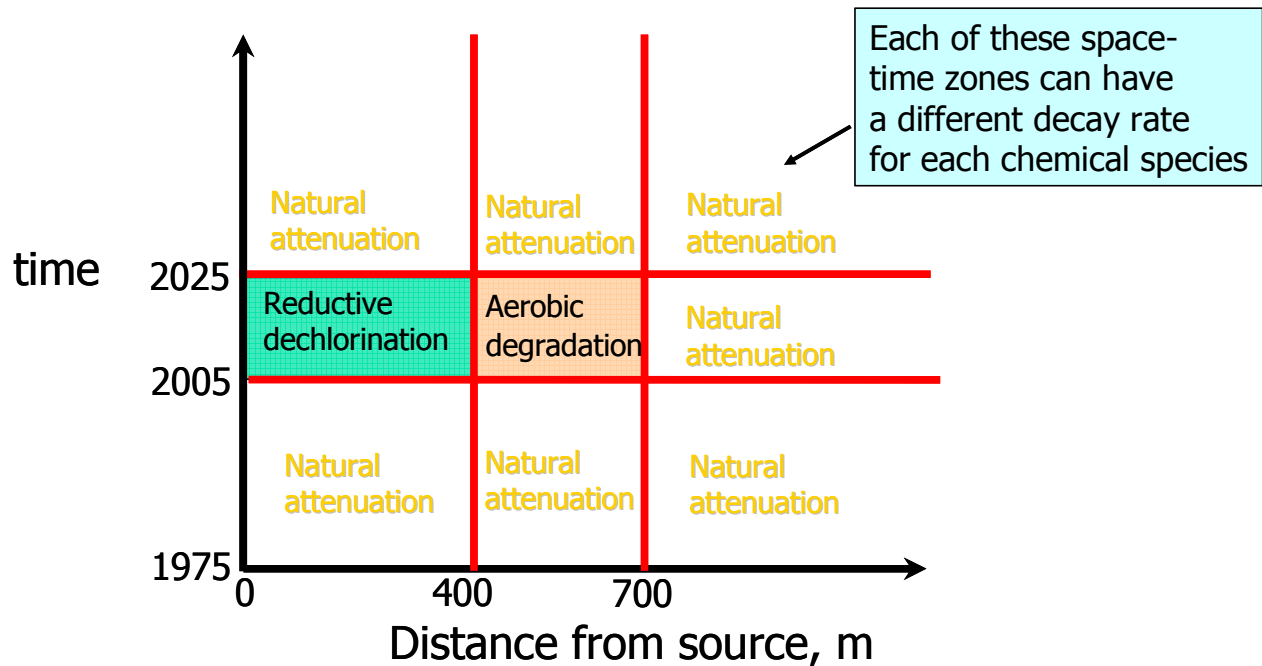


Figure 8. Possible design of an enhanced plume remediation scheme with an enhanced reductive chlorination zone for destruction of PCE and TCE, and an enhanced aerobic degradation zone for destruction of DCE and VC. All other zones revert to natural background (attenuation) conditions in this example.

The analytical solution for multiple reaction zones is developed using the residence time in each zone to develop the batch reaction solution for that zone. The initial conditions for the batch reaction are the final conditions from the previously encountered reaction zone. The residence times in each reaction zone are calculated using straightforward logic. For the example shown in Figure 7, the solutes that are present at location (x, t) left the source at a time, $t_{release}$ that was before t_1 , so they initially encounter reaction zone (I). The residence time in zone (I) is then $t_{(I)} = t_1 - t_{release}$. The solutes next enter zone (II), where they remain until they cross x_1 , at a time of $t_{release} + Rx_1/v$. Therefore, the residence time in zone (II) is $t_{(II)} = t_{release} + Rx_1/v - t_1$. The solutes next enter zone (V), where they remain until t_2 , so the residence time in zone (V) is $t_{(V)} = t_2 - t_{release} - Rx_1/v$. In this way, the residence times for each reaction zone are tabulated.

In general, solutes can pass through any of the nine reaction zones, so a total of nine reaction zone residence times are computed. For any given value of (x, t) , the advective path leading to that location will cross at most five zones, so several of the zone residence times are zero. The analytical solution is constructed by sequentially performing the batch reactions in each zone that is encountered, starting with

a concentration of $C(t_{release})|_{x=0}$. With the zone numbering scheme used in Figure 7, the numerical value of the reaction zone always increases with increasing travel distance.

Going back to the example of a single solute undergoing first order decay in the aqueous phase, a set of nine reaction rates are defined ($k_{(I)}-k_{(IX)}$). The solute concentration at (x,t) is then:

$$C(x,t) = C(t - Rx/v)|_{x=0} \exp \left\{ - \sum_{n=I}^{IX} \frac{t_{(n)} k_{(n)}}{R} \right\} \quad (22)$$

A problem of significant practical interest involves simultaneous first order parent-daughter decay/production reactions. Considering a four component system, the relevant batch reaction equations for species A,B,C,D in zones (n) are:

$$R \frac{dC_{A(n)}}{dt} = -k_{A(n)} C_{A(n)} \quad I.C. \rightarrow C_{A(n)}(0) = C_{A(n-1)} \quad (23)$$

$$R \frac{dC_{B(n)}}{dt} = y_{BA(n)} k_{A(n)} C_{A(n)} - k_{B(n)} C_{B(n)} \quad I.C. \rightarrow C_{B(n)}(0) = C_{B(n-1)} \quad (24)$$

$$R \frac{dC_{C(n)}}{dt} = y_{CB(n)} k_{B(n)} C_{B(n)} - k_{C(n)} C_{C(n)} \quad I.C. \rightarrow C_{C(n)}(0) = C_{C(n-1)} \quad (25)$$

$$R \frac{dC_{D(n)}}{dt} = y_{DC(n)} k_{C(n)} C_{C(n)} - k_{D(n)} C_{D(n)} \quad I.C. \rightarrow C_{D(n)}(0) = C_{D(n-1)} \quad (26)$$

where $y_{ij(n)}$ are the yield coefficients for each parent-daughter reaction. Theoretically, these can also depend on distance and time if the nature of a reaction changes so that it no longer produces the same proportion of daughter product from decay of the parent (for example during aerobic degradation of DCE, little VC is produced). Note, however, that in the current REMChlor coding, the yield coefficients are assumed to be constant in space and time. Equations (23-26) are written for reaction zone (n), and the reactions proceed for a period equal to the residence time, $t_{(n)}$, with initial conditions that are the concentrations from end of the previous reaction zone. The starting conditions for the first reaction zone are $C_{i(0)} = C_i(t - Rx/v)|_{x=0}$.

Following methods used in chemical reactor design (see, for example, Chen (1983)), the coupled reaction equations can be solved by Laplace transform methods to yield:

$$C_{A(n)} = C_{A(n-1)} f_1(\lambda_{A(n)}, t_{(n)}) \quad (27)$$

$$C_{B(n)} = C_{A(n-1)} f_2(\lambda_{A(n)}, \lambda_{B(n)}, y_{BA(n)}, t_{(n)}) + C_{B(n-1)} f_1(\lambda_{B(n)}, t_{(n)}) \quad (28)$$

$$C_{C(n)} = C_{A(n-1)} f_3(\lambda_{A(n)}, \lambda_{B(n)}, \lambda_{C(n)}, y_{BA(n)}, y_{CB(n)}, t_{(n)}) \\ + C_{B(n-1)} f_2(\lambda_{B(n)}, \lambda_{C(n)}, y_{BC(n)}, t_{(n)}) + C_{C(n-1)} f_1(\lambda_{C(n)}, t_{(n)}) \quad (29)$$

$$\begin{aligned}
C_{D(n)} = & C_{A(n-1)}f_4(\lambda_{A(n)}, \lambda_{B(n)}, \lambda_{C(n)}, \lambda_{D(n)}, y_{BA(n)}, y_{CB(n)}, y_{DC(n)}, t_{(n)}) \\
& + C_{B(n-1)}f_3(\lambda_{B(n)}, \lambda_{C(n)}, \lambda_{D(n)}, y_{CB(n)}, y_{DC(n)}, t_{(n)}) \\
& + C_{C(n-1)}f_2(\lambda_{C(n)}, \lambda_{D(n)}, y_{DC(n)}, t_{(n)}) + C_{D(n-1)}f_1(\lambda_{D(n)}, t_{(n)})
\end{aligned} \tag{30}$$

where the $\lambda_{i(n)} = k_{i(n)}/R$, and

$$f_1(\lambda_1, t) = e^{-\lambda_1 t} \tag{31}$$

$$f_2(\lambda_1, \lambda_2, y_{21}, t) = y_{21}\lambda_1 \left(\frac{e^{-\lambda_1 t} - e^{-\lambda_2 t}}{\lambda_2 - \lambda_1} \right) \tag{32}$$

$$f_3(\lambda_1, \lambda_2, \lambda_3, y_{21}, y_{32}, t) = y_{32}\lambda_2 y_{21}\lambda_1 \left(-\frac{(\lambda_3 - \lambda_2)e^{-\lambda_1 t} + (\lambda_1 - \lambda_3)e^{-\lambda_2 t} + (\lambda_2 - \lambda_1)e^{-\lambda_3 t}}{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_2)(\lambda_1 - \lambda_3)} \right) \tag{33}$$

$$\begin{aligned}
f_4(\lambda_1, \lambda_2, \lambda_3, \lambda_4, y_{21}, y_{32}, y_{43}, t) = & \frac{y_{43}\lambda_3 y_{32}\lambda_2 y_{21}\lambda_1}{(\lambda_2 - \lambda_1)(\lambda_4 - \lambda_3)} \left\{ \frac{e^{-\lambda_1 t} - e^{-\lambda_3 t}}{(\lambda_3 - \lambda_1)} - \frac{e^{-\lambda_1 t} - e^{-\lambda_4 t}}{(\lambda_4 - \lambda_1)} \right. \\
& \left. - \frac{e^{-\lambda_2 t} - e^{-\lambda_3 t}}{(\lambda_3 - \lambda_2)} + \frac{e^{-\lambda_2 t} - e^{-\lambda_4 t}}{(\lambda_4 - \lambda_2)} \right\}
\end{aligned} \tag{34}$$

These batch solutions are widely known as the Bateman equations (Bateman, 1910), originally developed to describe the decay and production of radioactive species. Here, the equations have been modified to account for variable daughter yield coefficients. These batch solutions are also equivalent to those developed by Sun et al. [1999] in their analytical transformations. Equations (32) – (34) become singular if identical decay rates are used for parent and daughter compounds. This can be avoided in practice by adjusting the rates slightly so that they are not exactly equal, and this is the approach that is used in the REMChlor code.

The new solution method is compared with the two-zone BIOCHLOR model in Figure 9. This case assumes a constant source concentration of PCE of 1 mg/l, with a pore velocity of 100 m/yr, a retardation factor of 2, and no dispersion. Referring back to Figure 7, this test case only uses zones (I) and (IV), with steady-state conditions in zone (I). This is a special case for the new solution, which can handle fully transient conditions using all nine zones in space and time.

Over the first 500 m, PCE and TCE are allowed to degrade with first order rate constants of 0.693/yr (an aqueous half life of one year), but DCE and VC do not degrade at all in this zone. Beyond 500 m, the DCE and VC degrade with a rate constant of 0.693/yr, but the PCE and TCE do not degrade at all. The simulation time of 20 years is sufficiently long for steady-state conditions to be present in the first zone, a requirement of the BIOCHLOR model. The two solutions produce an identical result. In the first zone, PCE degrades, producing TCE, which degrades into DCE. The process stalls at DCE in this zone, and the concentration of VC is zero. Beyond 500 m, the concentrations of PCE and DCE are constant, while the DCE degrades to form VC, which also degrades.

Longitudinal dispersion is included by considering a bundle of streamtubes that have a normally distributed velocity field, with a mean velocity of \bar{v} , and a velocity standard deviation of σ_v . This approach is similar to that used by Small (2003) in his streamtube transport model, except that he assumed a lognormal distribution of velocity.

For a given location, x , and time, t , a velocity of v^* is needed for the advective front to exactly reach that location. Assuming a normally distributed velocity field, the probability that a streamtube's velocity is less than v^* is (Abramowitz and Stegun, 1972)

$$P(v < v^*) = \frac{1}{\sigma_v \sqrt{2\pi}} \int_{-\infty}^{v^*} \exp\left(\frac{-(\tau - \bar{v})^2}{2\sigma_v^2}\right) d\tau = \frac{1}{2} \left(1 + \operatorname{erf}\left(\frac{v^* - \bar{v}}{\sigma_v \sqrt{2}}\right)\right) \quad (35)$$

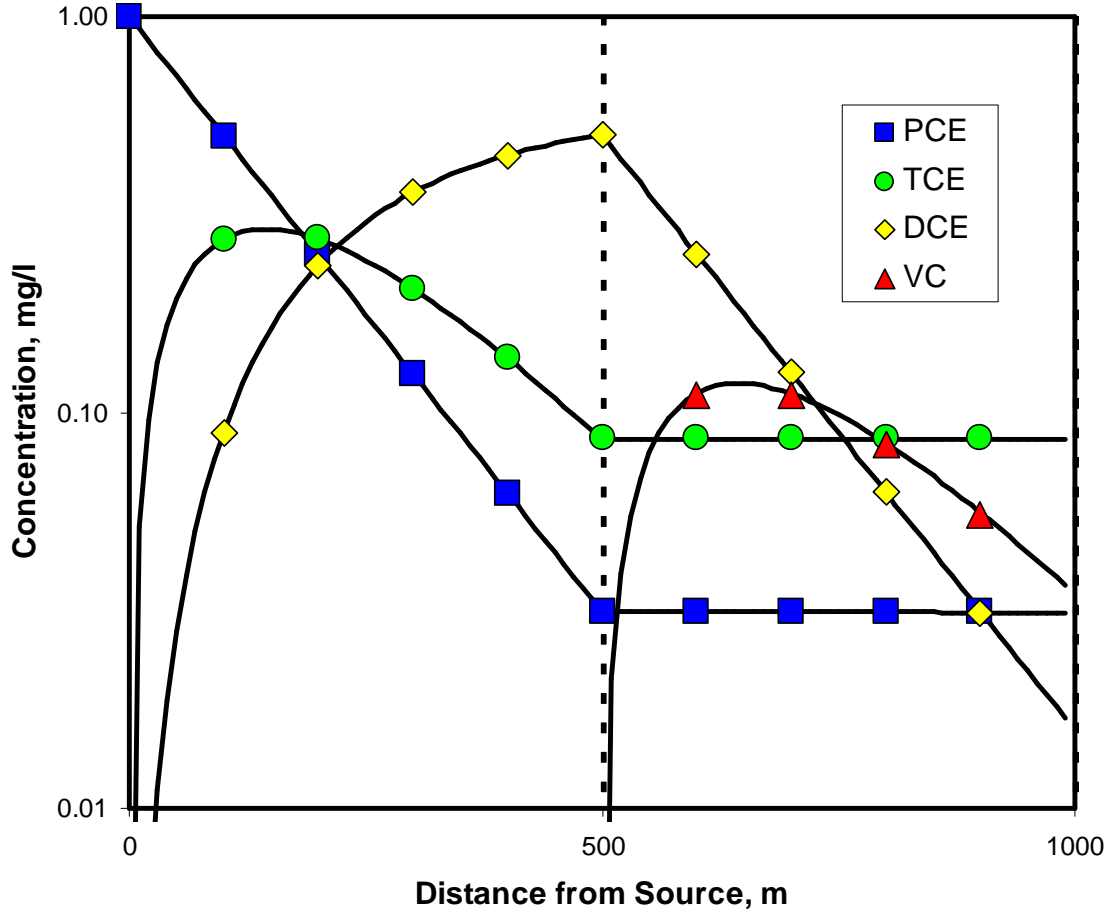


Figure 9. Comparison of REMChlor analytical solution with BIOCHLOR for a two-zone case with steady-state concentrations in the upstream zone. The solid lines are computed using REMChlor, while the symbols were calculated using BIOCHLOR.

This expression can be written in terms of travel distances at some time t by multiplying the relevant quantities in Equation (35) by t , and by using $x = \bar{v}t$. If the inlet concentration is fixed at a value of C_0 , then the concentration at (x, t) would be one minus the probability that the streamtube's advective front had not passed that location yet:

$$\frac{C}{C_0} = 1 - P(vt < v^*t) = 1 - \frac{1}{2} \left[1 + \operatorname{erf}\left(\frac{v^*t - \bar{v}t}{\sigma_v t \sqrt{2}}\right)\right] = \frac{1}{2} \operatorname{erfc}\left(\frac{x - \bar{v}t}{\sigma_v t \sqrt{2}}\right) \quad (36)$$

Equation (36) has the same form as the analytical solution to the one-dimensional advection dispersion equation in an infinite system where the initial concentration is C_0 for $x < 0$, and $C=0$ for $x > 0$ (Charbeneau, 2000):

$$\frac{C}{C_0} = \frac{1}{2} \operatorname{erfc} \left(\frac{x - \bar{v}t}{2\sqrt{\alpha_x \bar{v}t}} \right) \quad (37)$$

These two expressions are equivalent if the dispersivity in Equation (37) is

$$\alpha_x = \frac{\sigma_v^2}{2\bar{v}} t = \frac{\sigma_v^2}{2\bar{v}^2} \bar{x} = a\bar{x} \quad (38)$$

where \bar{x} is average front location, $\bar{v} t$. Therefore, the normally distributed velocity streamtube model produces a scale dependent dispersion solution, whose dispersivity is a linear function of the mean front location. One small drawback of this solution is that it does not exactly guarantee that the concentration at $x=0$ is C_0 , due to the infinite domain. This is generally a minor effect except at very large dispersivity values (Charbeneau, 2000). The same problem arises in the streamtube model, because with a normally distributed velocity distribution, some of the velocities would theoretically be negative. This effect would be more pronounced as the ratio of the standard deviation of velocity to the mean velocity becomes large.

The computational procedure for the streamtube dispersion model requires the specification of the number of streamtubes, n_{tubes} , mean and standard deviation of velocity, and the minimum and maximum velocities, v_{min} and v_{max} . The advective system is then divided into n_{tubes} with a velocity range for each tube calculated by

$$\Delta v = \frac{v_{max} - v_{min}}{n_{tubes}} \quad (39)$$

The probability that a streamtube, j , has a velocity within the range of $(v_j - \Delta v / 2) < v_j < (v_j + \Delta v / 2)$ is calculated from the probability function:

$$P(v_j < (v_j + \Delta v / 2)) - P(v_j < (v_j - \Delta v / 2)) \quad (40)$$

Beginning at $v_j - \Delta v / 2 = v_{min}$, each streamtube is assigned a weight, w_j equal to this probability. The longitudinal dispersion solution is constructed for each value of (x, t) by calculating the individual streamtube analytical solutions using the distributed velocities. All of the streamtubes are fed from the same source function that was described earlier. After all of the individual streamtube solutions have been calculated, they are weighted by the function defined by Equation (40), and summed to get the solution for advection with longitudinal dispersion.

The streamtube model is compared to Equation (37) in Figure 10 for a highly dispersive case, with $a=1/10$, and for an advection dominated case with $a=1/200$. The streamtube solution perfectly matches the analytical solution when a large number (a few hundred) of streamtubes are used, and it provides a reasonable approximation of the solution with as few as ten streamtubes. This method produces concentration profiles that are exactly symmetrical around the mean advective front. The profiles do not change with distance scales if the x -axis is normalized to the mean front location, due to the linear scale dependency of dispersivity.

As mentioned earlier, these solutions can produce a relative concentration at $x=0$ that is slightly less than one. For the highly dispersive case shown here, the relative concentration at $x=0$ was 0.987, so the magnitude of this effect is small for practical values of dispersivity. An attractive feature of the approach is that for small values of x , the dispersive flux approaches zero, so the flux boundary condition, Equation (10), can be satisfied by just using the advective flux term.

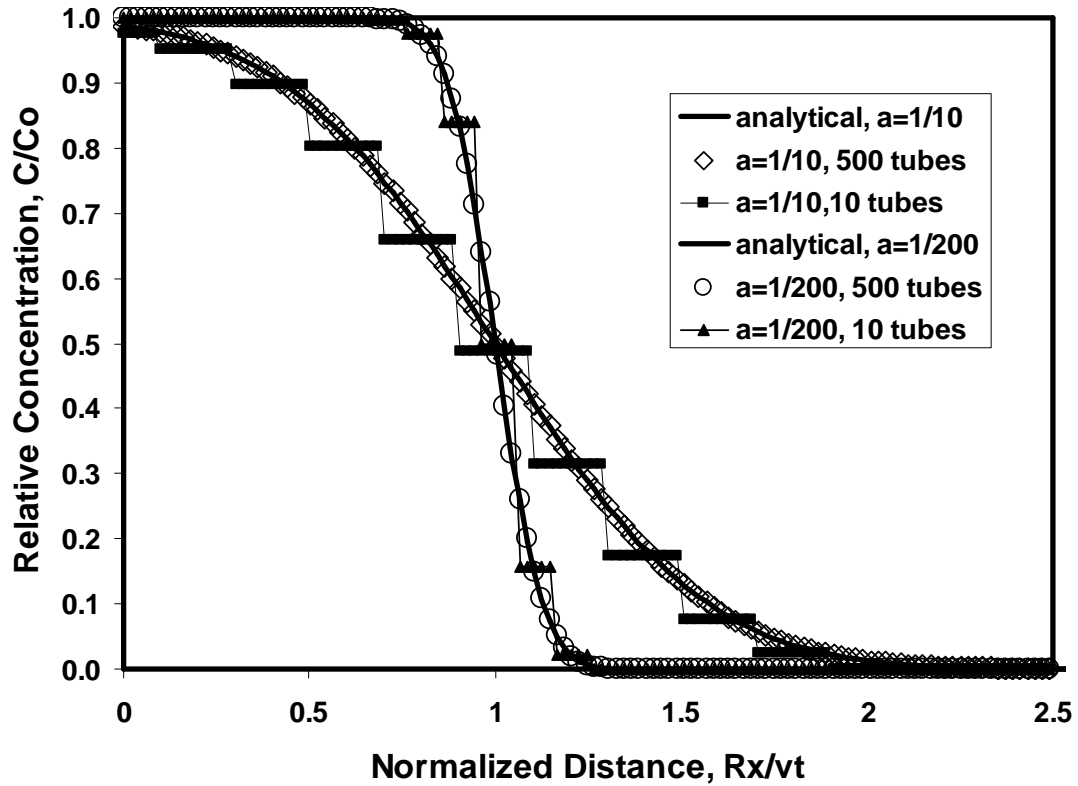


Figure 10. Comparison of REMChlor streamtube dispersion model to error function analytical solution using a scale dependent dispersivity equal to $\alpha_x = a\bar{x}$.

The total mass discharge of the dissolved species crossing a downgradient control plane can be computed directly from the streamtube solution by simply summing the individual streamtube discharges, using the weighting function, Equation (40).

The effects of transverse and vertical dispersion are included using Domenico's (1987) approximation. With this method, the solution with three-dimensional dispersion is constructed from the one-dimensional solution:

$$C(x, y, z, t) = C(x, t) f_y(y) f_z(z) \tag{41}$$

where the transverse and vertical functions are

$$f_y(y) = \frac{1}{2} \left(\operatorname{erf} \left\{ \frac{y+Y/2}{2\sqrt{\alpha_y x}} \right\} - \operatorname{erf} \left\{ \frac{y-Y/2}{2\sqrt{\alpha_y x}} \right\} \right) \quad \text{and}$$

$$f_z(z) = \frac{1}{2} \left(\operatorname{erf} \left\{ \frac{z+Z}{2\sqrt{\alpha_z x}} \right\} - \operatorname{erf} \left\{ \frac{z-Z}{2\sqrt{\alpha_z x}} \right\} \right) \quad (42)$$

This formulation assumes a rectangular source zone with dimensions of Y by Z , with dispersion occurring in the positive and negative y directions, but only in the positive z direction. Equation (42) can be altered to allow vertical dispersion in both directions (Domenico and Schwartz, 1990).

The accuracy of the Domenico transverse dispersion approximation has recently been called into question. West et al. [2007] and Srinivasan et al. [2007] show that use of the Domenico approximation in problems with very large longitudinal dispersivities can lead to substantial errors in the predicted concentrations compared to the exact solution of Wexler [1992] or Cleary and Ungs [1978]. Although West et al. [2007] recommend using only the exact transverse dispersion solutions, these models suffer from two important limitations. First, the exact dispersion solutions only apply to specific limited boundary conditions at $x=0$, and they cannot be easily adapted to other more general boundary conditions. Second, they are not closed form solutions, and they require numerical evaluation of integrals [Srinivasan et al., 2007]. As Srinivasan et al. [2007] have pointed out, the Domenico approximation offers a simple method for extending 1-D solutions to 3-D, and the error involved in this approximation is small as long as dispersivity values are small.

The REMChlor model was compared to an exact analytical solution for reactive transport with advection and 2-D dispersion (Figure 11). This analytical solution applies to the case of a continuous point source located at the origin that injects a specified mass rate (kg/yr) into the plume over time. If the solute undergoes decay in the plume, the plume will stabilize at a finite distance, and can be modeled using a steady-state assumption. From Charbeneau [2000], the analytical solution for a continuous point source at steady state is:

$$C(x, y, t) = \frac{\dot{m} \exp\left(\frac{x}{2\alpha_x}\right)}{2\pi\phi Z v \sqrt{\alpha_x \alpha_y}} K_0\left(\frac{r}{B}\right) \quad (43)$$

with

$$r^2 = \frac{x^2}{\alpha_x v / R} + \frac{y^2}{\alpha_y v / R} \quad (44)$$

and

$$B^2 = \frac{1}{\frac{k}{R} + \frac{v}{4\alpha_x R}} \quad (45)$$

where \dot{m} is the rate of mass injection into the plume, Z is the vertical thickness over which the mass is injected, v is the pore velocity, ϕ is the porosity, k is the first order decay rate in the plume, and α_x and α_y are the longitudinal and transverse dispersivities, respectively. The term $K_0(r/B)$ is a Modified Bessel Function of order zero.

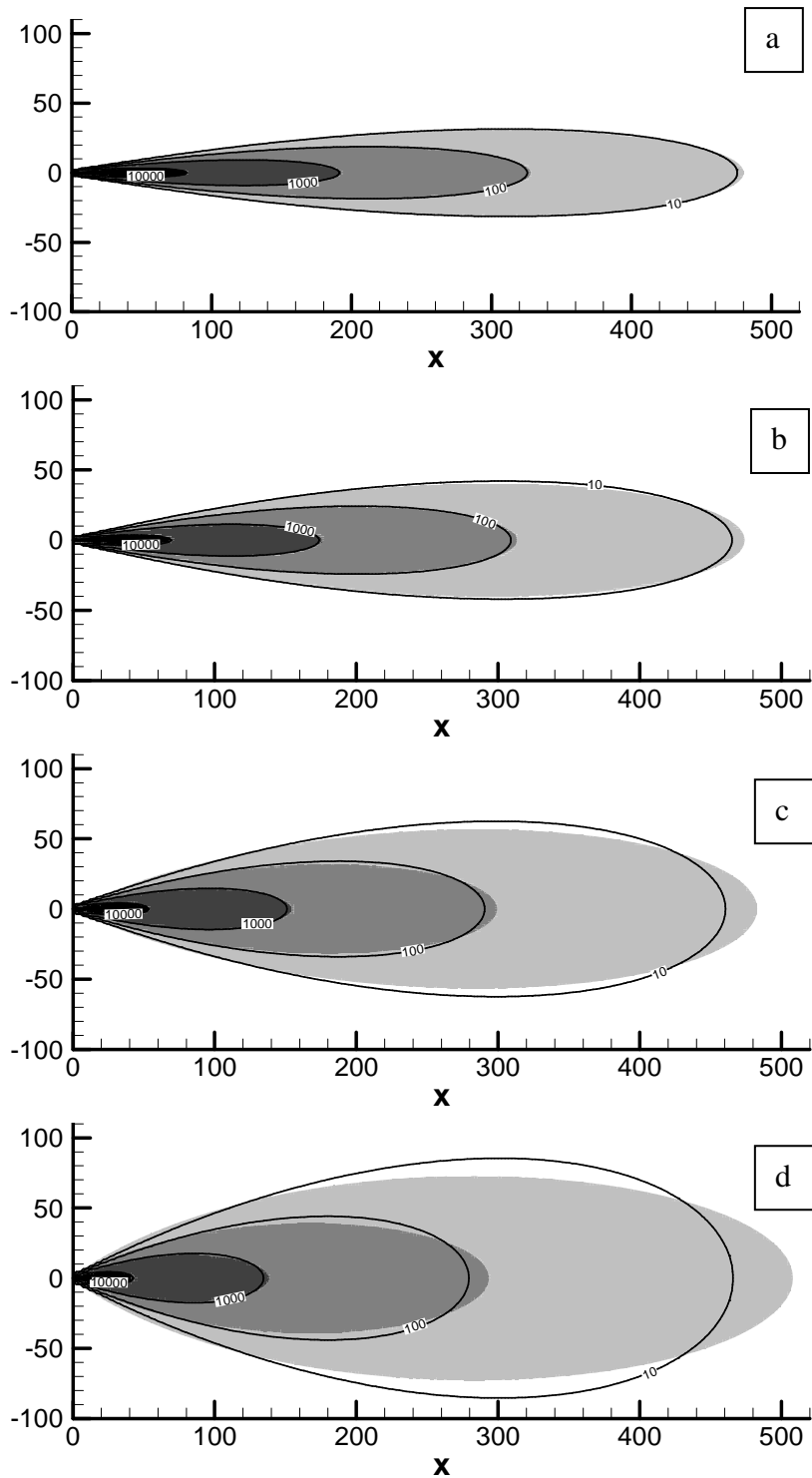


Figure 11. Comparison of REMChlor (solid lines) with exact analytical solution (shaded) for $\alpha_x = x/100$ (a), $x/50$ (b), $x/20$ (c), and $x/10$ (d) with $\alpha_y = \alpha_x / 10$. Concentration units are ug/l.

The comparison in Figure 11 is for a case where the mass injection rate is 2 kg/yr, the pore velocity is 10 m/yr, the solute half-life in the plume is 5 years, and the retardation factor is one. The longitudinal dispersivity is varied from 1/100 to 1/10 of the travel distance, and the transverse dispersivity (α_y) is 1/10 of the longitudinal value. The REMChlor model assumes a finite, rectangular source region at $x=0$, and for this reason, it cannot exactly represent the infinitely small point source used in the exact analytical solution. As long as the source rectangle in REMChlor is “small”, this error is only evident over the first few m of transport.

The cases with $\alpha_x = x/100$ and $x/50$ (Figure 11a, b) show almost perfect agreement between the two solutions. As the dispersivities are increased, the difference in the two solutions becomes evident. For the very large dispersivity case ($\alpha_x = x/10$, Figure 11d), the outer contour of the steady-state plume calculated using the Domenico approximation occurs at about 90% of the distance calculated using the exact model. This outer concentration contour is also about 10-15% wider than the exact model result..

For sites with large dispersivities, one could evaluate the potential magnitude of the dispersion error from the Domenico approximation using the new BIOSCREEN-AT program [Karanovic et al., 2007]. BIOSCREEN-AT is a modified version of BIOSCREEN that includes the exact solution to the 3-D dispersion problem for constant or exponentially decaying source terms at $x=0$. The REMChlor model uses streamtubes to simulate longitudinal dispersion, with the Domenico approximation employed only for lateral and vertical dispersion. Although the REMChlor longitudinal model uses a scale-dependent dispersivity, a comparison of BIOSCREEN with BIOSCREEN-AT for a similar set of parameter values would likely show whether the error in the Domenico approximation was significant for that case.

Calculation of Cancer Risk

Many of the regulated groundwater contaminants and their degradation products are considered to be known or probable carcinogens by the US EPA. Cancer risk from exposure to carcinogens is quantified using the chronic daily intake (*CDI*) of the carcinogen (mg/kg-day) and a cancer risk slope factor (*SF*) that has units of risk per mg/kg-day. The *CDI* is a dose rate averaged over a human lifespan, regardless of the exposure period (US EPA, 1989). The maximum exposure period, t_{ex} is usually limited to 30 years. The risk is calculated as

$$Risk = 1 - \exp(-CDI \times SF) \quad (46)$$

which for small risks is equivalent to (US EPA, 1989)

$$Risk = CDI \times SF \quad (47)$$

The total carcinogenic risk, $Risk_T$, from exposure to multiple carcinogens (for example PCE, TCE, and VC) is calculated as the sum of the individual risks (US EPA, 1989)

$$Risk_T = \sum Risk_i \quad (48)$$

A major exposure route for contaminated groundwater is water from wells in the dissolved plume area. The contaminants contained in the water may be ingested directly, in drinking water, and if they are volatile, they may be inhaled as the contaminant partitions from the water into the air in the house (McKone, 1987). The cancer risk from inhalation is often as large or larger than the risk from ingestion alone (McKone, 1987; Williams et al., 2004).

The CDI for both ingestion (CDI_G) and inhalation (CDI_H) is computed using the well water concentration in mg/L averaged over the maximum exposure period,

$$\bar{C}_w(t) = \frac{1}{t_{ex}} \int_{\max(0, t-t_{ex})}^t C_w(\tau) d\tau \quad (49)$$

The lower limit in the integral restricts the exposure period to a maximum of t_{ex} . The upper limit, t , is the time since the contaminant release occurred. Once the average tap water concentration is known, the ingestion and inhalation cancer risks can be calculated using standard methods (see, for example, Maxwell et al. (1998); McKone (1987); Williams et al. (2004)).

The cancer risk from water ingestion assumes a daily water intake of q_w L/d, and a body mass of m kg. Then using the standard life expectancy, t_{life} , the CDI_G is

$$CDI_G = \bar{C}_w \left(\frac{q_w \times t_{ex}}{m \times t_{life}} \right) \quad (50)$$

Typical values for q_w , m , and t_{life} are 2 L/d, 70 kg, and 70 years, respectively. The ingestion risk is then

$$Risk_G = 1 - \exp(-CDI_G \times SF_G) \quad (51)$$

where SF_G is the oral slope factor for the carcinogen.

Calculation of the inhalation exposure requires estimation of indoor air concentrations of the carcinogen that result from water use in the house. The standard approach is to separately consider the shower stall, the bathroom, and the remainder of the house (McKone, 1987). An empirical water to gas transfer efficiency (TE) is used to relate the contaminant mass flowrate in water passing through parts of the house (shower, bathroom, house) to the rate of mass loading in the indoor air. Based on extensive data sets collected for radon gas exposure, the TE for a volatile chemical is computed from the radon data with a correction for the different Henry's constant and aqueous and gaseous diffusion rates. Of these parameters, the TE is most sensitive to the aqueous diffusion rate, because that tends to limit the rate of mass transfer into indoor air (McKone, 1987). Typical values for TE are in the range of 0.3 to 0.9, depending mainly on the nature of the water use (for example a shower versus a dishwasher).

The CDI_H is computed separately for the three main compartments (shower, bathroom, house) using the average indoor air concentration of the carcinogen, \bar{C}_a in units of mg/m³. For compartment k , this concentration is calculated from the average water concentration using the tap water use rate W_k (L/hr), the TE_k , and the air exchange rate, VR_k (m³/hr):

$$\bar{C}_{a,k} = \bar{C}_w \left(\frac{W_k \times TE_k}{VR_k} \right) \quad (52)$$

The CDI_H for each compartment ($CDI_{H,k}$) depends on the daily exposure time in the compartment, ET_k (hr/d), and the inhalation rate, HR (m³/hr):

$$CDI_{H,k} = \bar{C}_{a,k} \left(\frac{ET_k \times HR \times t_{ex}}{m \times t_{life}} \right) \quad (53)$$

The risk from inhalation sums over the compartments

$$Risk_H = 1 - \exp \left[- \sum_k CDI_{H,k} \times SF_H \right] \quad (54)$$

where SF_H is the inhalation slope factor.

The lifetime excess cancer risk slope factors vary widely among different chemicals, they are often revised or withdrawn. Conflicting values of SF can be found in different sources in many instances. Table 1 lists current (as of February, 2006) recommended inhalation and oral slope factors for PCE, TCE, and VC from the California Office of Environmental Health Hazard Assessment (OEHHA, 2006). Values of other risk-related parameters used in REMChlor are shown in Table 2.

Table 1. California cancer risk slope factors for PCE and its degradation products (OEHHA, 2006).

Chemical	Inhalation Slope Factor (mg/kg-day) ⁻¹	Oral Slope Factor (mg/kg-day) ⁻¹
Tetrachloroethylene (PCE)	0.021	0.540
Trichloroethylene (TCE)	0.007	0.013
Cis-1,2-Dichloroethylene (DCE)	-not a carcinogen	-not a carcinogen
Vinyl chloride (VC)	.270	0.270

Table 2 Exposure parameters used in cancer risk calculations.

Exposure Parameter	Value
Human life span, yrs	70 ¹
Body mass, kg	70
Exposure duration, yrs	30 ¹
Daily water intake, L/d	2
Inhalation rate, m ³ /d	13.25 ²
Water use rate, shower, L/hr	480 ¹
Water use rate, bathroom, L/hr	40 ¹
Water use rate, house, L/hr	40 ¹
Transfer efficiency, shower	0.5 ¹
Transfer efficiency, bathroom	0.43 ¹
Transfer efficiency, house	0.43 ¹
Air exchange rate, shower, m ³ /hr	12 ¹
Air exchange rate, bathroom, m ³ /hr	55 ¹
Air exchange rate, house, m ³ /hr	750 ¹
Exposure time, shower, hr/d	0.17 ¹
Exposure time, bathroom, hr/d	0.32 ¹
Exposure time, house, hr/d	15.9 ¹

¹Mean value from Maxwell et al. (1998)

²USEPA (1997)

Model Limitations

1. Model assumes homogeneous and constant groundwater velocity field with flow in one direction.
2. The contaminant source mass balance assumes that the contaminant discharge is a power function of the remaining contaminant mass using an exponent Γ . This is a simplistic model of a complicated heterogeneous multiphase transport system, and the best value of Γ for a given site will be subject to a range of uncertainty. For this reason, it is probably a good idea to run the model with a range of Γ values.
3. The model assumes that biodegradation reactions in the plume can be described by first order decay reactions. The biogeochemical conditions that control these reactions may not be well represented by first order reactions, and there is considerable uncertainty in values of field scale decay rates.
4. All of the dissolved solutes (parent and daughter compounds) are assumed to have the same retardation coefficient (R), so they move at the same velocity.
5. First order decay rates are a function of time and distance from the source (x), but they do not depend on the y or z coordinates. This means that a specified reaction zone will extend over the entire model domain in the y and z directions.
6. The model uses a conventional advection-dispersion formulation, and is not able to account for transient diffusion into low permeability zones in the plume. Diffusion of contaminants into low permeability zones may result in plume rebound after the source is depleted to back diffusion.
7. Transverse and vertical dispersion are approximated using the Domenico [1987] method. This can lead to errors in the concentration distributions, particularly when large dispersion coefficients are used (see Figure 11).

Graphical User Interface

Projects Tab

When REMChlor is started (by double clicking on the application icon), the default project, “Sample”, is seen in the title window. Here is where the user may define the project name and file location.

Once the project name is double-clicked, the tab becomes “REMChlor Project” and the parameter entry screen is shown.

Parameter Entry

This section allows parameter entry for setting up the entire model run. The various model input variables are described in the next section

Options for Viewing Model Output

View File Output

The text files created by the model may be viewed in either Notepad (the .inp and .out files) or Excel (the .csv files).

View Graphical Output

Concentration, Mass Discharge or Risk Factor versus distance for any value of time, t can be viewed graphically by clicking on “Output vs Distance” under “View Graphical Output”. This puts the user in a window where model output is seen graphically. The user also has access to a powerful and comprehensive suite of graphical tools.

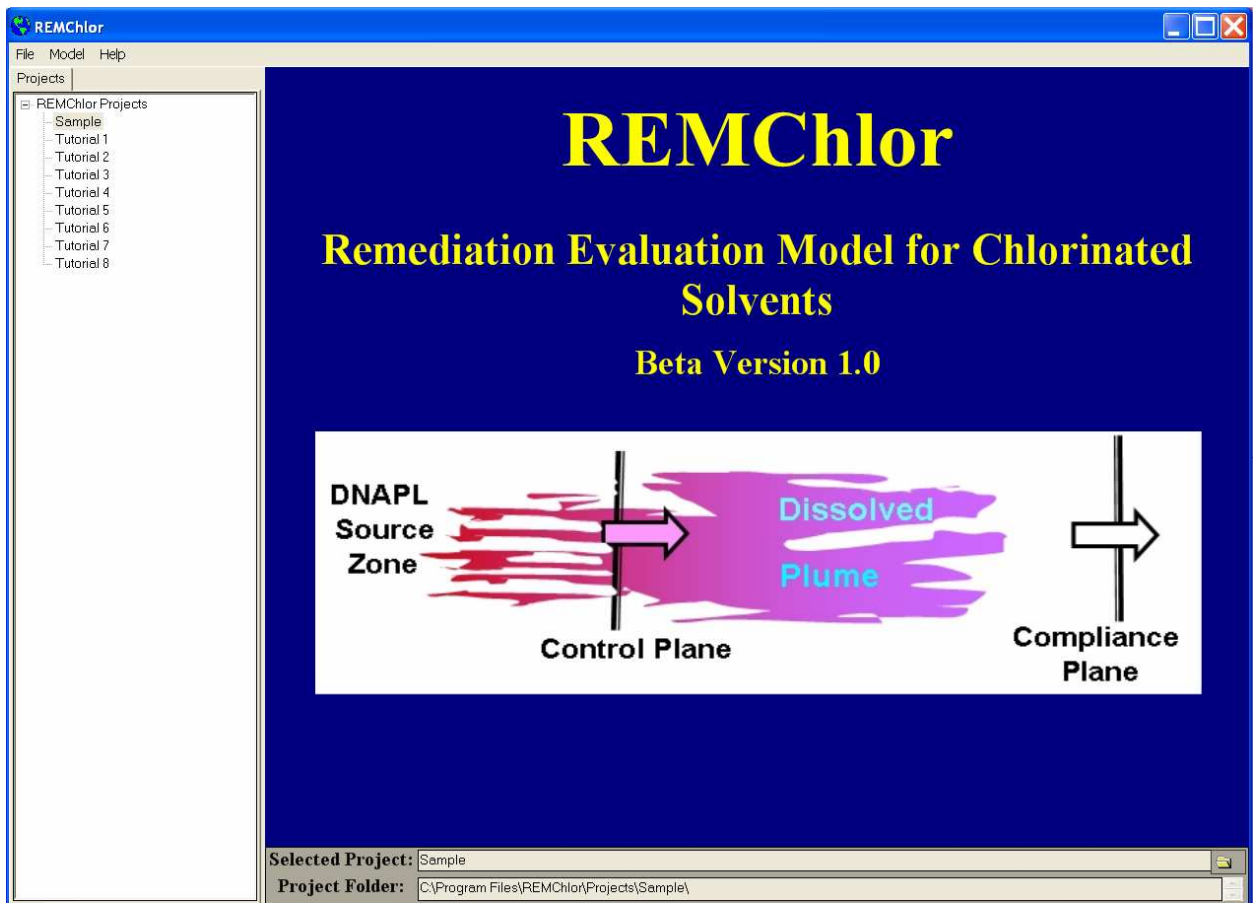
If the model was set up with more than one Y-Interval and/or Y- and Z-Intervals, a 2-D x-y contour map can be displayed by clicking on “2D Contour” under “View Graphical Output”. This puts the user in a window that is similar to the one for “Output vs Distance”, where model output is seen as a

concentration, risk factor, or mass discharge contour map in the x-y plane. The user here has access to the same powerful and comprehensive suite of graphical tools.

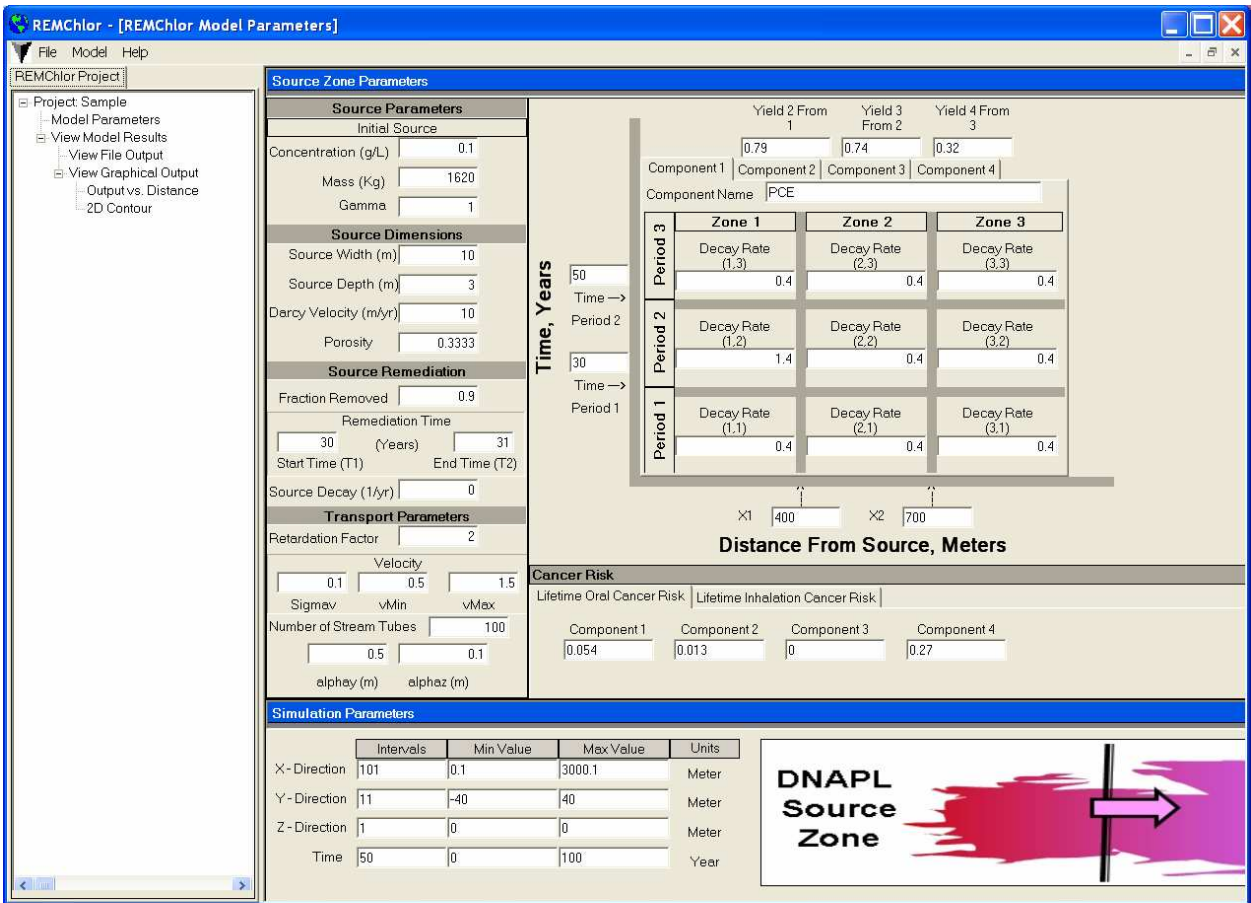
Basic Operation

The following simple tutorial exercise illustrates the most basic functions and capabilities of the graphical user interface for REMChlor. It uses the “Sample” project file that comes with the model.

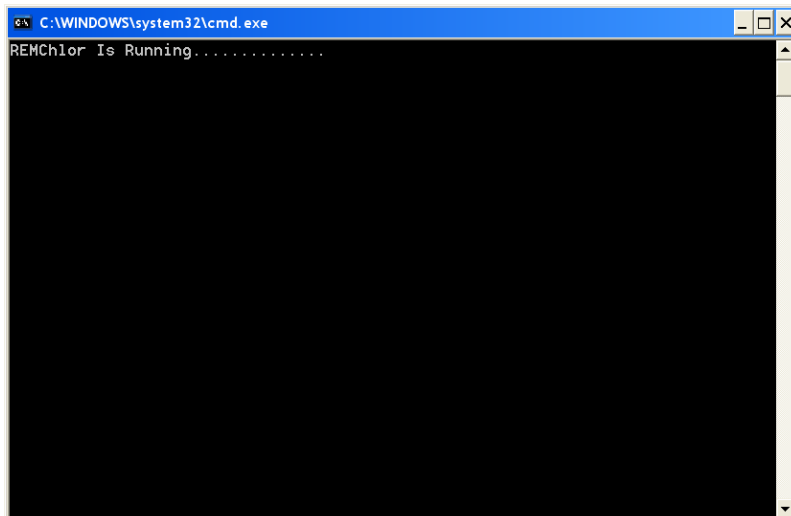
1. Double-click the REMChlor icon on your desktop to start the application. You will see the following screen:



- Double-click on “Sample” under REMChlor Projects and you will see the Model Parameters screen. As you move the mouse over the input boxes, a simple explanation of the input is provided in pop-up boxes.



- The parameters are set to run the Sample problem. Make the following changes in the ‘Simulation Parameters’ box at the bottom of the window: X-Direction Max Value = 2000.1; Y-Direction Min Value = -100 and Max Value = 100. From the Model pull-down menu, click “Run”. The following screen will appear.



4. After completion of the run, you may “View File Output” or “View Graphical Output” simply by clicking on one of these options under “View Model Results”. The following screen will appear if “View File Output” is selected (this is the “Sample.inp” file, which is the formatted text file used as the input to the FORTRAN code that computes the analytical solution).

```

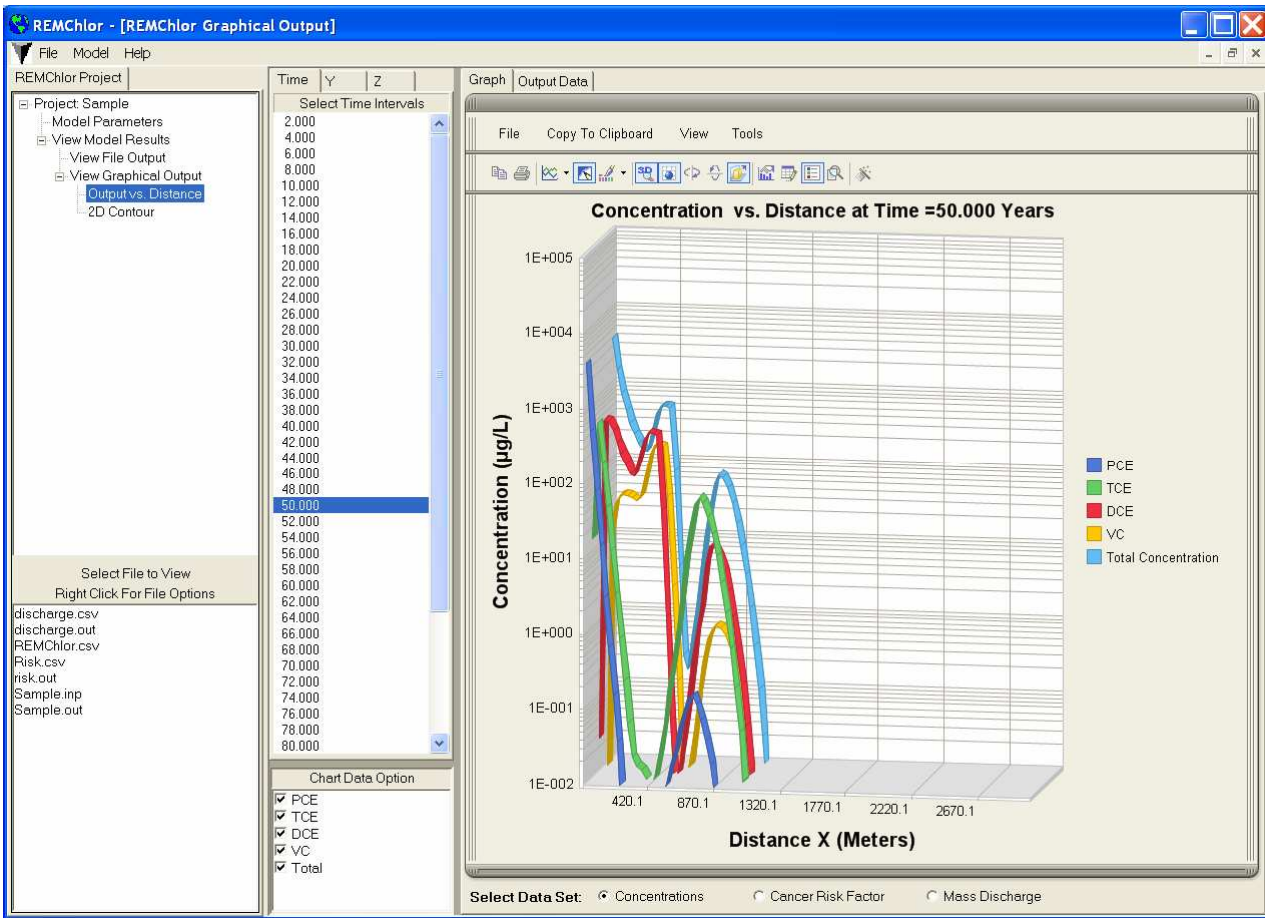
REMChlor Project
  Project: Sample
    Model Parameters
    View Model Results
      View File Output
      View Graphical Output
        Output vs. Distance
        2D Contour

Select File to View
Right Click For File Options
discharge.csv
discharge.out
REMChlor.csv
Risk.csv
Risk.out
Sample.inp
Sample.out

***source zone parameters
czero (g/l), tzeromass (kg), gamma, xremove, t1, t2
0.1, 1620., 1., 0.9, 30., 31.
***source zone parameters
rates (1/yr), ysource (m), zsource (m), vd (m/yr)
0., 10., 3., 10.
***transport and streamtube velocity parameters
porosity, retard, sigmav, vmin, vmax, ntubes, alphas (m), alphaz (m)
0.3333, 2., 0.1, 0.5, 1.5, 100, 0.5, 0.1
***distance to end of zone 1 and zone 2 for plume remediation
x1, x2 (m)
400., 700.
***length of period 1 and period 2 for plume remediation
tplume1, tplume2 (yr)
30., 50.
***lifetime cancer risk oral slope factors, per (mg/kg) per day
slopef(1), slopef(2), slopef(3), slopef(4)
0.054, 0.013, 0., 0.27
***lifetime cancer risk inhalation slope factors, per (mg/kg) per day
slopef(1), slopef(2), slopef(3), slopef(4)
0.021, 0.007, 0., 0.27
***yield coefficients for chain reactions
yield21, yield32, yield43
0.79, 0.74, 0.32
***11COMPONENT 1 plume decay rate constants in zone 1 for 3 time periods **111**
ratep(1,1,1), ratep(1,1,2), ratep(1,1,3) (1/yr)
0.4, 1.4, 0.4
***COMPONENT 1 plume decay rate constants in zone 2 for 3 time periods
ratep(1,2,1), ratep(1,2,2), ratep(1,2,3) (1/yr)
0.4, 0.4, 0.4
***COMPONENT 1 plume decay rate constants in zone 3 for 3 time periods
ratep(1,3,1), ratep(1,3,2), ratep(1,3,3) (1/yr)
0.4, 0.4, 0.4
***22COMPONENT 2 plume decay rate constants in zone 1 for 3 time periods **222**
ratep(2,1,1), ratep(2,1,2), ratep(2,1,3) (1/yr)
0.15, 1.5, 0.15
***COMPONENT 2 plume decay rate constants in zone 2 for 3 time periods
ratep(2,2,1), ratep(2,2,2), ratep(2,2,3) (1/yr)
0.15, 0.15, 0.15
***COMPONENT 2 plume decay rate constants in zone 3 for 3 time periods
ratep(2,3,1), ratep(2,3,2), ratep(2,3,3) (1/yr)
0.15, 0.15, 0.15
***33COMPONENT 3 plume decay rate constants in zone 1 for 3 time periods **333**
ratep(3,1,1), ratep(3,1,2), ratep(3,1,3) (1/yr)
0.1, 0.2, 0.1
***COMPONENT 3 plume decay rate constants in zone 2 for 3 time periods
ratep(3,2,1), ratep(3,2,2), ratep(3,2,3) (1/yr)
0.1, 3.5, 0.1
***COMPONENT 3 plume decay rate constants in zone 3 for 3 time periods
ratep(3,3,1), ratep(3,3,2), ratep(3,3,3) (1/yr)
0.1, 0.1, 0.1

```

- Clicking on “Output vs Distance” under “View Graphical Output”, and selecting Time Interval 50 will bring up the following screen. Within this window, the user has access to a fully functioning suite of user-friendly and powerful graphics tools for viewing, and saving output images.

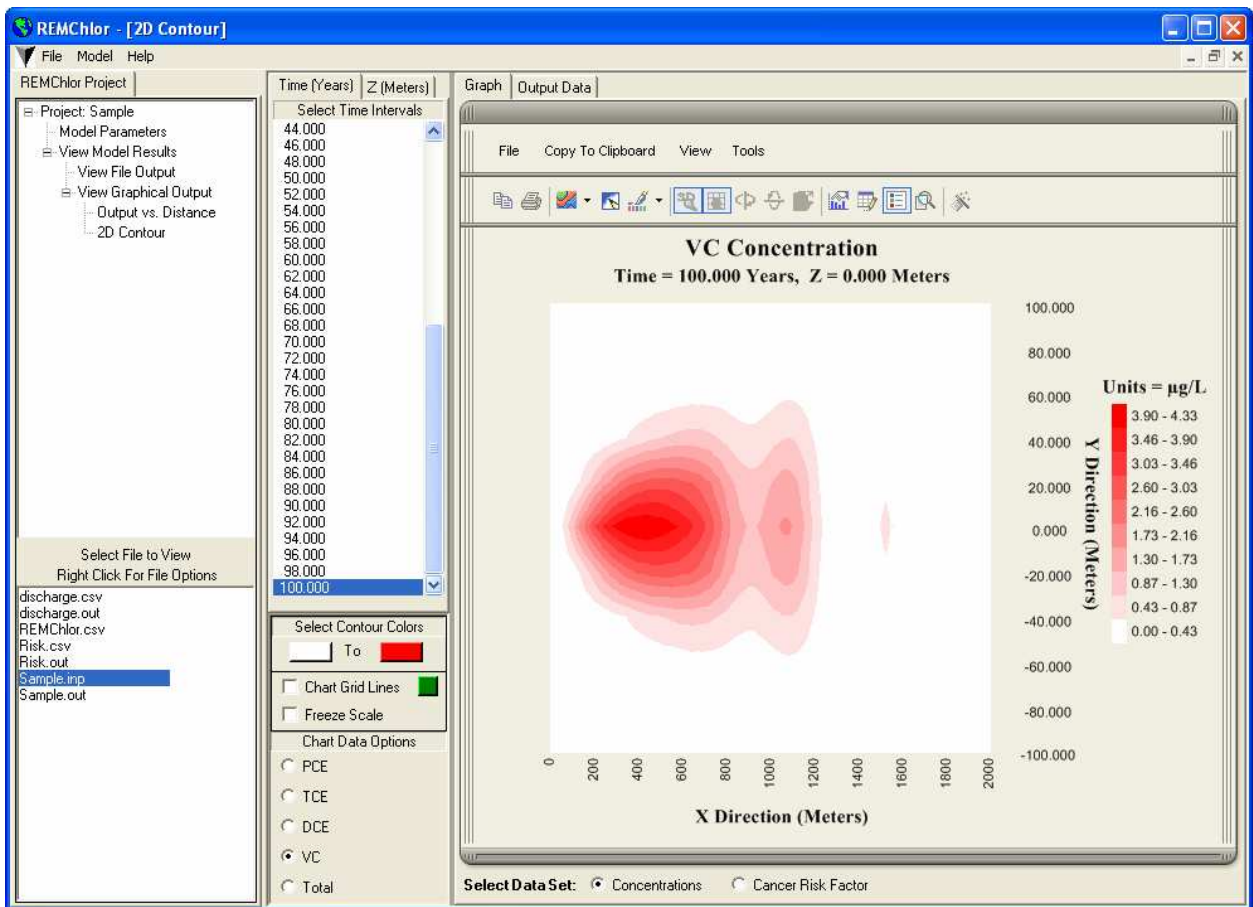


6. Clicking on the “Output Data” tab above the graph will display the raw data used to create the graph:

The screenshot shows the REMChlor graphical user interface. The main window displays the 'Output Data' tab, which contains a table of raw data. The table has columns for Time, x, y, z, PCE, TCE, DCE, and VC. The data is organized into rows, with the first row highlighted. The 'Time' column shows values of 50 for all rows. The 'x', 'y', and 'z' columns show increasing values from 0.1 to 660.1. The 'PCE', 'TCE', 'DCE', and 'VC' columns show various numerical values, including scientific notation.

Time	x	y	z	PCE	TCE	DCE	VC
50	0.1	0	0	4017.01	14.9575	0.0282914	2.0807E
50	20.1	0	0	1025.29	735.033	375.34	6.3434E
50	40.1	0	0	264.11	362.36	515.535	19.690E
50	60.1	0	0	78.399	154.855	479.878	30.735E
50	80.1	0	0	25.2831	64.0133	399.459	37.612E
50	100.1	0	0	8.60658	26.2204	320.337	40.971E
50	120.1	0	0	3.04524	10.7293	254.485	41.859E
50	140.1	0	0	1.10975	4.40084	202.606	41.156E
50	160.1	0	0	0.414079	1.81226	162.397	39.491E
50	180.1	0	0	0.157557	0.749818	131.274	37.304
50	200.1	0	0	0.0609613	0.311844	107.399	35.060E
50	220.1	0	0	0.023958	0.130561	91.3763	34.163E
50	240.1	0	0	0.00965826	0.0557985	90.3783	39.258E
50	260.1	0	0	0.00428721	0.0263637	119.766	59.2731
50	280.1	0	0	0.00255247	0.0168218	187.147	99.0001
50	300.1	0	0	0.00216105	0.0149244	269.438	146.64E
50	320.1	0	0	0.00200627	0.0141571	327.755	181.48E
50	340.1	0	0	0.00172373	0.0123325	346.232	194.70E
50	360.1	0	0	0.00136597	0.0099129	338.724	193.50E
50	380.1	0	0	0.00104171	0.00768737	322.62	187.20E
50	400.1	0	0	0.000789316	0.00594469	302.445	179.16E
50	420.1	0	0	0.00113514	0.0102764	31.9759	39.400E
50	440.1	0	0	0.00163798	0.0179278	3.54658	6.4195E
50	460.1	0	0	0.0023718	0.0316788	0.41129	0.9589E
50	480.1	0	0	0.00344594	0.0569221	0.0511741	0.1395E
50	500.1	0	0	0.00502264	0.104442	0.00957513	0.0211E
50	520.1	0	0	0.00734332	0.196533	0.00727405	0.0049E
50	540.1	0	0	0.0107631	0.379624	0.0126462	0.0044E
50	560.1	0	0	0.0157981	0.750617	0.0248319	0.0081E
50	580.1	0	0	0.023223	1.52211	0.0503575	0.0163E
50	600.1	0	0	0.0339765	3.07606	0.101809	0.0330E
50	620.1	0	0	0.0492236	6.1105	0.202301	0.0656E
50	640.1	0	0	0.0711282	12.2817	0.406705	0.1319E
50	660.1	0	0	0.099311	22.7186	0.752431	0.2441E

7. Clicking on “2D Contour” under “View Graphical Output” will bring up the 2D contour map screen. If you put a check in the “VC” box and look at time = 100, the screen will show the vinyl chloride plume at 100 years. The graphical results can be saved in the project file for later viewing or printing.



Model Input Variables

DNAPL Source Parameters and Dimensions

Source Parameters – Initial Source (t=0)

Source Zone Parameters	
Source Parameters	
Initial Source	
Concentration (g/L)	0.1
Mass (Kg)	1620
Gamma	1
Source Dimensions	
Source Width (m)	10
Source Depth (m)	3
Darcy Velocity (m/yr)	10
Porosity	0.3333

Concentration = initial source zone concentration; C_o , flow averaged concentration of DNAPL chemical leaving the source zone, g/l

Mass = initial source zone contaminant mass, M_o , kg

Gamma = power function exponent Γ in source concentration versus mass function, equation (2). A value of zero results in a constant source concentration with time until the source is depleted. A value of one results in an exponentially decaying source concentration. In most cases Γ should probably be between 0.5 and 2, with the lower value more likely to occur at younger sites, and the higher value at older sites. When Γ is set equal to 1, REMChlor automatically resets it to a value of 1.01 in order to avoid the singularity in Equation (5). Due to the uncertainty in this parameter, it is a good idea to run the code with a range of values to assess the range of possible impacts.

Source Width = source zone width, Y , m

Source Depth = vertical thickness of source zone, Z , m

Darcy Velocity = Darcy flux (velocity), V , in the flow system. The unretarded chemical velocity, (pore velocity, v) is the Darcy velocity divided by the porosity. The total flow rate through the source zone, $Q=VYZ= \phi vYZ$. Darcy velocity units are m/yr

Porosity = effective porosity, ϕ

Source Remediation

Source Remediation	
Fraction Removed	<input type="text" value="0.9"/>
Remediation Time	
<input type="text" value="30"/> (Years)	<input type="text" value="31"/>
Start Time (T1)	End Time (T2)
Source Decay (1/yr)	<input type="text" value="0"/>

Percent Removed = Fraction, X of source mass at time t_1 that is removed by source remediation activities. $0 \leq X \leq 1$

Start Time = Time when source remediation begins, t_1 , years

End Time = Time when source remediation ends, t_2 , years

Source Decay = First order source decay rate by processes other than dissolution and flushing, λ_s . This might include biological or chemical reactions in the source zone that destroy source mass, 1/yr

Transport Parameters

Source Remediation	
Fraction Removed	<input type="text" value="0.9"/>
Remediation Time	
<input type="text" value="30"/> (Years)	<input type="text" value="31"/>
Start Time (T1)	End Time (T2)
Source Decay (1/yr)	<input type="text" value="0"/>

Retardation Factor = Retardation factor for all dissolved species (must be equal to each other), R . Typically estimated from organic carbon partition coefficient and soil fraction of organic carbon.

$\text{Sig}mav$ = Coefficient of variation for velocity field, equal to the ratio of the pore velocity standard deviation, divided by the mean pore velocity, σ_v / \bar{v} .

This results in a scale-dependent dispersivity (Equation 38) that is equal to $\frac{1}{2}(\text{sig}mav)^2 \bar{x}$, where \bar{x} is the average front location at a given time. See also Figure 10, and tutorial example 2. A $\text{sig}mav$ value of 0.1 results in a longitudinal dispersivity equal to 1/200 of the travel distance; a $\text{sig}mav$ value of 0.44721 results in a longitudinal dispersivity equal to 1/10 of the travel distance. The table below gives $\text{Sig}mav$ values corresponding to different longitudinal dispersivities:

α_x	$\text{Sig}mav$
$x/200$	0.1
$x/100$	0.14142
$x/50$	0.2
$x/20$	0.31623
$x/10$	0.44721

$vMin$ = minimum normalized streamtube velocity (see Equation 39). Typically set equal to 0, except when very small $\text{sig}mav$ is used. In that case, v_{min} can be somewhat larger (e.g. 0.5), and still effectively capture the full velocity range. Ideally, v_{min} and v_{max} would be symmetrical around 1, but this is limited by the restriction that v_{min} must be positive. This parameter truncates the lower range of the velocity distribution.

$vMax$ = maximum normalized streamtube velocity (see Equation 39). Magnitude depends on $\text{sig}mav$, and $vMax=1+4*\text{Sig}mav$ is suggested for most cases. This parameter truncates the higher range of the velocity distribution.

Number of Stream Tubes = number of streamtubes used to simulate longitudinal dispersion. The more tubes used, the smoother the solution will look, but the longer it will take to compute; problem execution time is directly proportional to the number of streamtubes used. A solution calculated with only 10 streamtubes may still represent the dispersion reasonably well (see Figure 10), but it will not be “smooth”. A solution calculated with 500 streamtubes will be smoother, but it will take 50 times longer to compute. *In general, the problem run time in seconds is roughly equal to the number of stream tubes times the number of x locations where the solution is evaluated, times the number of times when the solution is evaluated, divided by ~200,000.*

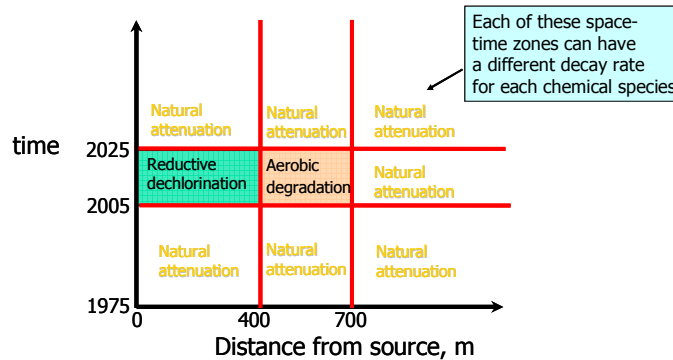
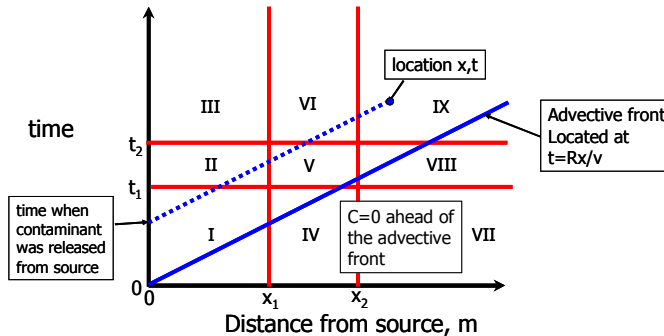
alphay = Transverse dispersivity, α_y , constant value in m. This is generally 1/10 or less of the effective longitudinal value. If a negative number is entered, the dispersivity is calculated as the absolute value of alphay times distance from the source, x .

α_z = Vertical dispersivity, α_z , constant value in m. This is generally 1/100 or less (perhaps much less) of the effective longitudinal value. If a negative number is entered, the dispersivity is calculated as the absolute value of α_z times distance from the source, x .

Plume Decay Rates and Yield Coefficients

The plume reaction parameters are entered using a table that mimics the distance-time reaction graph, Figures 7 and 8. Note that in the model, time starts at zero, when the DNAPL spill occurs, at location $x=0$. The 9 different reaction rates must be entered separately for each of the 4 chemical species using the “component #” tabs. As each tab is selected, the component name can be entered, along with the table of 9 first order decay rates (that vary in distance and time).

Component 1 is always the ultimate parent compound, and it is the component that is released from the DNAPL source zone. Component 2 is produced from the decay of component 1, and it decays to produce component 3. Component 3 decays to produce component 4. Component 4 is assumed to decay into a harmless species.



Yield Coefficients

		Yield 2 From 1		Yield 3 From 2		Yield 4 From 3		
		0.79		0.74		0.32		
		Component 1	Component 2	Component 3	Component 4			
		Component Name PCE						
Time, Years	Period 3	Zone 1		Zone 2		Zone 3		
		Decay Rate (1,3)		Decay Rate (2,3)		Decay Rate (3,3)		
		0.4		0.4		0.4		
	Period 2	Decay Rate (1,2)		Decay Rate (2,2)		Decay Rate (3,2)		
		1.4		0.4		0.4		
		Decay Rate (1,1)		Decay Rate (2,1)		Decay Rate (3,1)		
	0.4		0.4		0.4			
	Period 1		Decay Rate (1,1)		Decay Rate (2,1)		Decay Rate (3,1)	
	0.4		0.4		0.4			
		X1 400		X2 700				
		Distance From Source, Meters						

Yield 2 From 1 = Mass of component 2 created by first order decay of one unit of mass of component 1, y_{21} . Typically, for reductive dechlorination, this would be the molecular weight of component 2 divided by the molecular weight of component 1. If component 1 decays without producing any important daughter products, this yield coefficient would be zero.

Yield 3 From 2 = Mass of component 3 created by first order decay of component 2, y_{32} . Typically, for reductive dechlorination, this would be the molecular weight of component 3 divided by the molecular weight of component 2. If component 2 decays without producing any important daughter products, this yield coefficient would be zero.

Yield 4 From 3 = Mass of component 4 created by first order decay of component 3, y_{43} . Typically, for reductive dechlorination, this would be the molecular weight of component 4 divided by the molecular weight of component 3. If component 3 decays without producing any important daughter products, this yield coefficient would be zero.

Plume Reaction Zones

The nine possible plume reaction zones are defined by entering two times, and two distances

		Yield 2 From 1	Yield 3 From 2	Yield 4 From 3
		0.79	0.74	0.32
		Component 1	Component 2	Component 3
		Component 4		
		Component Name PCE		
Time, Years		Zone 1	Zone 2	Zone 3
	50 Time →	Decay Rate (1,3)	Decay Rate (2,3)	Decay Rate (3,3)
		0.4	0.4	0.4
	Period 2	Decay Rate (1,2)	Decay Rate (2,2)	Decay Rate (3,2)
	30 Time →	1.4	0.4	0.4
	Period 1	Decay Rate (1,1)	Decay Rate (2,1)	Decay Rate (3,1)
		0.4	0.4	0.4
		X1 400	X2 700	
Distance From Source, Meters				

Time Period 1 = Defines the time, t_I when plume reaction rates change from their initial value (which started at $t=0$). Note that this time is unrelated to the time of source remediation. Units are years.

Time Period 2 = Defines the time, t_{II} when plume reaction rates change from their previous value (which started at $t=t_I$). Note that this time is also unrelated to the time of source remediation. Units are years. The third time period occurs after t_{II} .

X_I = Defines the first distance zone for reaction rates, m.

X_2 = Defines the second distance zone for reaction rates, m. The third zone occurs beyond X_2 .

Plume Species First Order Decay Rates

A total of 36 first order reaction rates are entered in the tables: 9 for each species. A separate table for each species is pulled up by clicking the appropriate "Component #" tab. Then the 9 different reaction rates can be entered for that component. All rates have units of 1/yr. The first component is the "parent" compound, while the remaining components are the successive "daughter" compounds. For the PCE reductive dehalogenation decay chain, the components 1-4 would be listed in the order PCE-TCE-DCE-VC.

The model is highly sensitive to the plume decay rates. Some useful references for data on "typical" values for differing conditions include Suarez and Rifai (1999), Chapelle et al. (1996), and Aziz et al. (2002).

Cancer Risk Parameters

Cancer Risk			
Lifetime Oral Cancer Risk		Lifetime Inhalation Cancer Risk	
Component 1	Component 2	Component 3	Component 4
0.054	0.013	0	0.27

Two sets of excess cancer risk slope factors are entered for each component: one for ingestion (drinking the water), and one for inhalation (breathing vapors in the shower, bathroom, and house). Note that direct vapor transport through the vadose zone is not included here. The units for the slope factors are risk per mg contaminant per kg body weight per day. Equations 43-51 outline the cancer risk calculations used in the program.

Simulation Output Parameters

Simulation Parameters				
	Intervals	Min Value	Max Value	Units
X - Direction	101	0.1	3000.1	Meter
Y - Direction	11	-40	40	Meter
Z - Direction	1	0	0	Meter
Time	50	0	100	Year

X - Direction = Enter the number of x values desired (intervals), and the minimum and maximum values of x used for plotting. **The minimum x value should be greater than zero (the solution is singular at x=0).** The problem run time is a linear function of the number of x intervals specified, but this has no effect on solution accuracy. The maximum number of x values is 200. *In general, the problem run time in seconds is roughly equal to the number of stream tubes times the number of x locations where the solution is evaluated, times the number of times when the solution is evaluated, divided by ~200,000.*

Y - Direction = Enter the number of y values desired (intervals), and the minimum and maximum values of y used for plotting. This is mainly used for producing x-y contour plots. The maximum number of y values is 50. If only center-line plots are needed, the number of y intervals can be set to 1, with the min and max value equal to 0. The model run time depends somewhat on the number of y-direction values calculated.

Z - Direction = Enter the number of *z* values desired (intervals), and the minimum and maximum values of *z* used for plotting. This is mainly used for producing *x-y-z* or *x-z* contour plots. If only center-line plots are needed, the number of *z* intervals can be set to 1, with the min and max value equal to 0. Note that $z=0$ corresponds to the plane of the vertical no flow boundary for dispersion; this location gives the maximum concentration at a given *x-y* location. Also, the well water concentration used in the cancer risk exposure integral (Equation 46) averages the values between z_{min} and z_{max} .

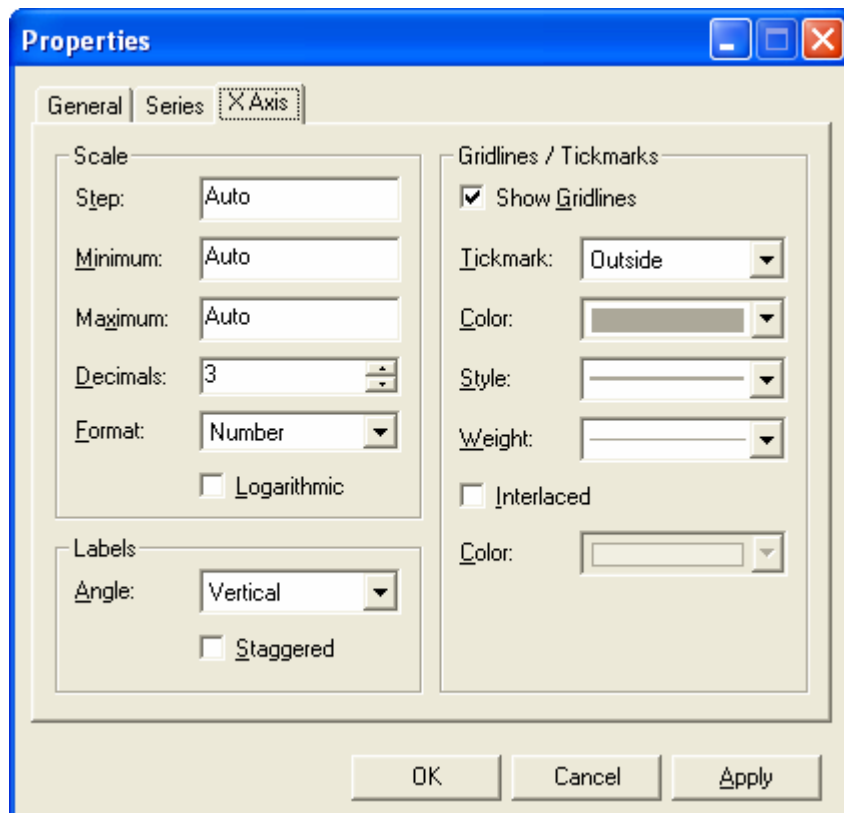
Time = Enter the number of *time* values desired (intervals), and the minimum and maximum values of *time* used for plotting. The problem run time is a linear function of the number of *time* intervals specified, but this has no effect on the concentration solution accuracy. However if cancer risk calculations are being performed, the exposure integral in Equation 46 is computed numerically using the trapezoidal rule. In this case sufficient time intervals are needed to accurately compute the integral. Considering a typical exposure period of 30 years, a time spacing of 2 or 3 years gives reasonable accuracy. Note also that the minimum time should be either 0, or at least 30 years prior to the time of the first risk calculation. Time starts when the DNAPL spill occurs, and the maximum number of time values is 100.

Tutorials

Getting Started

REMChlor has a total of eight tutorials. It will automatically load the files required to run the tutorials. Users need to select any tutorial from the GUI, and run the model from the drop-down menu “Model | Run”. Once the model has run, the various output files are created. The REMChlor graphics are accessed by clicking “View Graphical Output”, which allows the user to view concentration, mass discharge, or cancer risk plots.

The graphics package in REMChlor is very flexible, and the plot formatting can easily be changed by right clicking on the X-axis or Y-axes and selecting Properties.



Once a nice format for a particular plot has been created, it can be saved using the “file” command in the graph window. This file command can also be used to open a previously saved graph format. The graph files have extensions of .cfx, and the old data in the graphs can be updated by simply clicking on a time interval in the pane located to the left of the graph. The time selected in this pane can be toggled to quickly see the behavior of the system through time (almost like an animation of the plots).

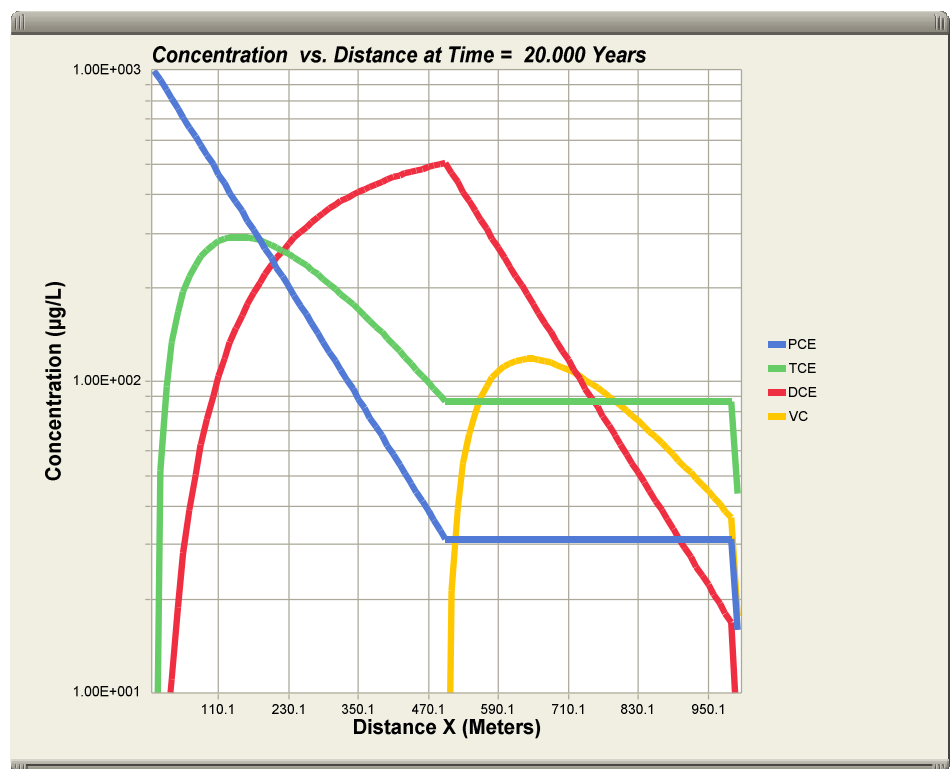
Tutorial 1: One-Dimensional Reactive Transport of PCE, TCE, DCE, and VC with 2 Reaction Zones, and No Dispersion or Remediation (BIOCHLOR Comparison)

This problem was described earlier in the REMChlor Analytical Mathematical Model section. It involves a constant release of dissolved PCE from the source zone, at a concentration of 1 mg/l (0.001 g/l). The source is made constant by selecting $\Gamma=0$. Dispersion is neglected by making all of the relevant variables ($\Sigma\sigma$, α , and α_{haz}) very small.

Since this problem does not involve any changes to the plume decay rates with time, the time values used to define Period 1 and Period 2 in the plume decay section are arbitrary.

The Distance From Source locations, however are important here, because this example uses two reaction (redox) zones in space. This was specified by setting X_1 equal to 500 m. In this example, the value of location X_2 does not matter, because the same decay rates are used in location zones 2 and 3. Note, however, that the decay rates in Zone 1 and Zone 2 are different for each of the four species.

After running this model, select “View Graphical Output”. Then click “file-Open Chart” in the plot window, and select the file “tutorial1.cfx”. Click on the time 20 years to see a plot similar to Figure 9 in the mathematical model section:



When you are done with a problem, you may choose “file-close project” to close the project, and move to a different problem.

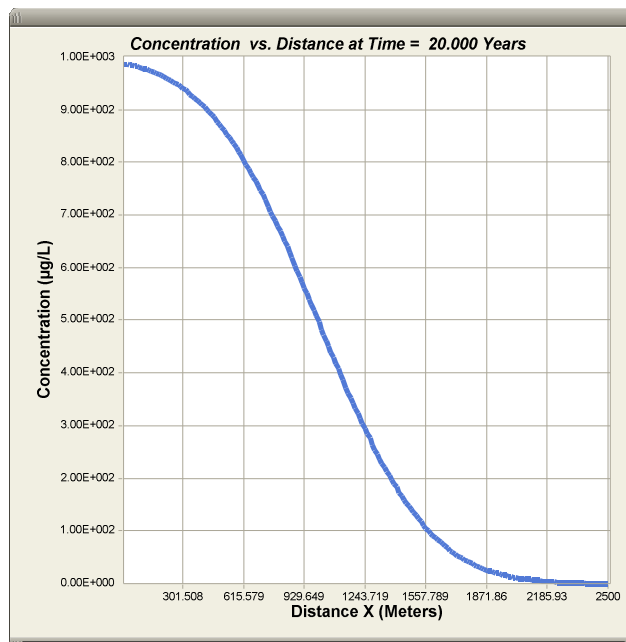
Tutorial 2: One-Dimensional Advection-Dispersion of a Non-Reactive Species

This problem was also described earlier in the REMChlor Analytical Mathematical Model section (Figure 10). It also involves a constant release of dissolved PCE from the source zone, at a concentration of 1 mg/l (0.001 g/l). The source is made constant by selecting $\Gamma=0$. Transverse and vertical dispersion are neglected by making variables α_{xy} and α_{yz} very small. The longitudinal dispersion is controlled by the variable Σ_{mv} , which is the coefficient of variation of the velocity field (see Equation 38). This formulation gives a scale-dependent dispersivity, with a dispersivity equal to $\frac{1}{2}(\Sigma_{mv})^2$ times the mean travel distance.

The Σ_{mv} value in this example of 0.44721 gives a longitudinal dispersivity of 0.1 times the travel distance. This would be considered a very high level of dispersion. Because of the wide range of groundwater velocities in this case, v_{Min} and v_{Max} are chosen to be further from one, and v_{Min} is set to the limiting value of 0. A value of 500 was used for the number of stream tubes in order to produce a smooth solution. In most practical cases, this is not necessary, and fewer stream tubes will produce a valid (but less smooth) solution.

Decay of the plume in this example is ignored by setting all of the plume decay rates equal to 0. The time period and distance from source variables are therefore arbitrary.

After running the problem, the formatted plot file “tutorial2.cfx” can be opened. At 20 years, the curve should look like:



Tutorial 3: Natural Attenuation of a TCA DNAPL Source and Dissolved Plume

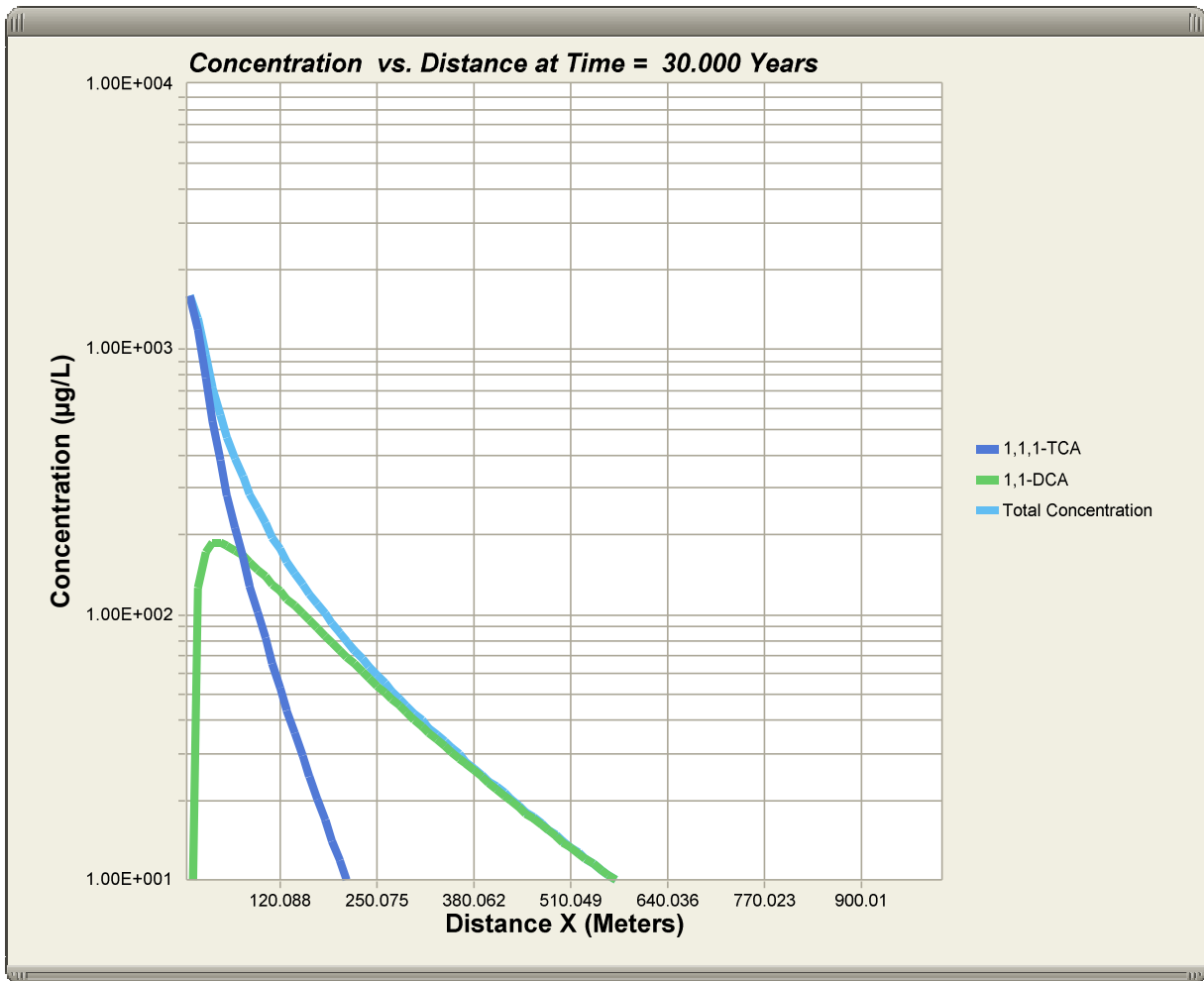
This is a more realistic application involving a 300 kg release of 1,1,1-trichloroethane (TCA) into an aquifer with a groundwater darcy velocity of 20 m/yr, and a porosity of 0.333. The source has dimensions of $Y=10$ m and $Z=3$ m so the total flowrate through the source zone is 600 m³ per year. The source is assumed to behave according to Equation (2), with an exponent, Γ , of 2. This type of source behavior tends to result in fairly rapid decreases in source strength at early times, followed by extensive tailing at later times (Falta et al., 2005a). The release was assumed to have occurred in 1975, and the initial source concentration (C_0) was specified as 2 mg/l, leading to an initial source discharge of 1.2 kg of TCA per year.

The TCA is assumed to undergo reductive dechlorination to 1,1-DCA, but at a slow rate of 0.8/yr. The 1,1-DCA also degrades, but at an even slower rate of 0.2/yr. These rates would be representative of sites where the rate of natural attenuation is weak (Aziz et al., 2002). Because this example does not include any variation of decay rates in space or time, all of the decay rates in the plume reaction plane are set equal, and the time period and zone distances are arbitrary. Alternatively, this model could be set up so with a very large Period 1 time, and a very large Zone 1 distance. In that case, the model would only encounter the lower left (Zone 1, Period 1) set of parent-daughter reaction rates. Note that only a single daughter product is considered in this simulation, because the second and third yield parameters (Yield 3 From 2 and Yield 4 From 3) were set to zero.

The compounds were assigned a retardation factor of 2, the longitudinal dispersivity is equal to 0.005 times the travel distance (a Sigma_v of 0.1), the transverse dispersivity is 0.5 m, and the vertical dispersivity is 0.1m. Neither TCA or 1,1-DCA are considered to be carcinogens, and the federal drinking water standard for TCA is 200 ug/l (there is no federal standard for 1,1-DCA). Since these are not carcinogens, the cancer risk calculations are not used, and all of the slope factors are set equal to zero.

In this example, we have transverse and vertical dispersion, and we are going to use external software (TECPLOTTM) to make 2-D contour plots using the REMChlor output files. For this reason, we have specified 41 intervals in the y-direction, with a Min Value of -60 m, and a Max Value of 60 m. If we wanted to make 3-D plots, we would also specify intervals in the z-direction. By choosing $z=0$, we have selected the plane at the base (or top) of the DNAPL zone, where it is assumed that there is no vertical dispersion (dispersion occurs in the other direction). This plane will always contain higher concentrations than planes with larger z values.

This model takes 15 seconds or more (depending on the clock speed of your computer's CPU) to run because of the large number of x,y,t values selected, and because 100 streamtubes were used. After running, a formatted concentration plot may be created by opening the file tutorial3.cfx in the plot window. At a time of 30 years (the year 2005), the plot should look like this:



The default setting for these plots chooses the plume center-line, at $y=0$ and $z=0$; however, any other value of y or z may be chosen for the plot using the Y and Z tabs at the top of the plot selection pane.

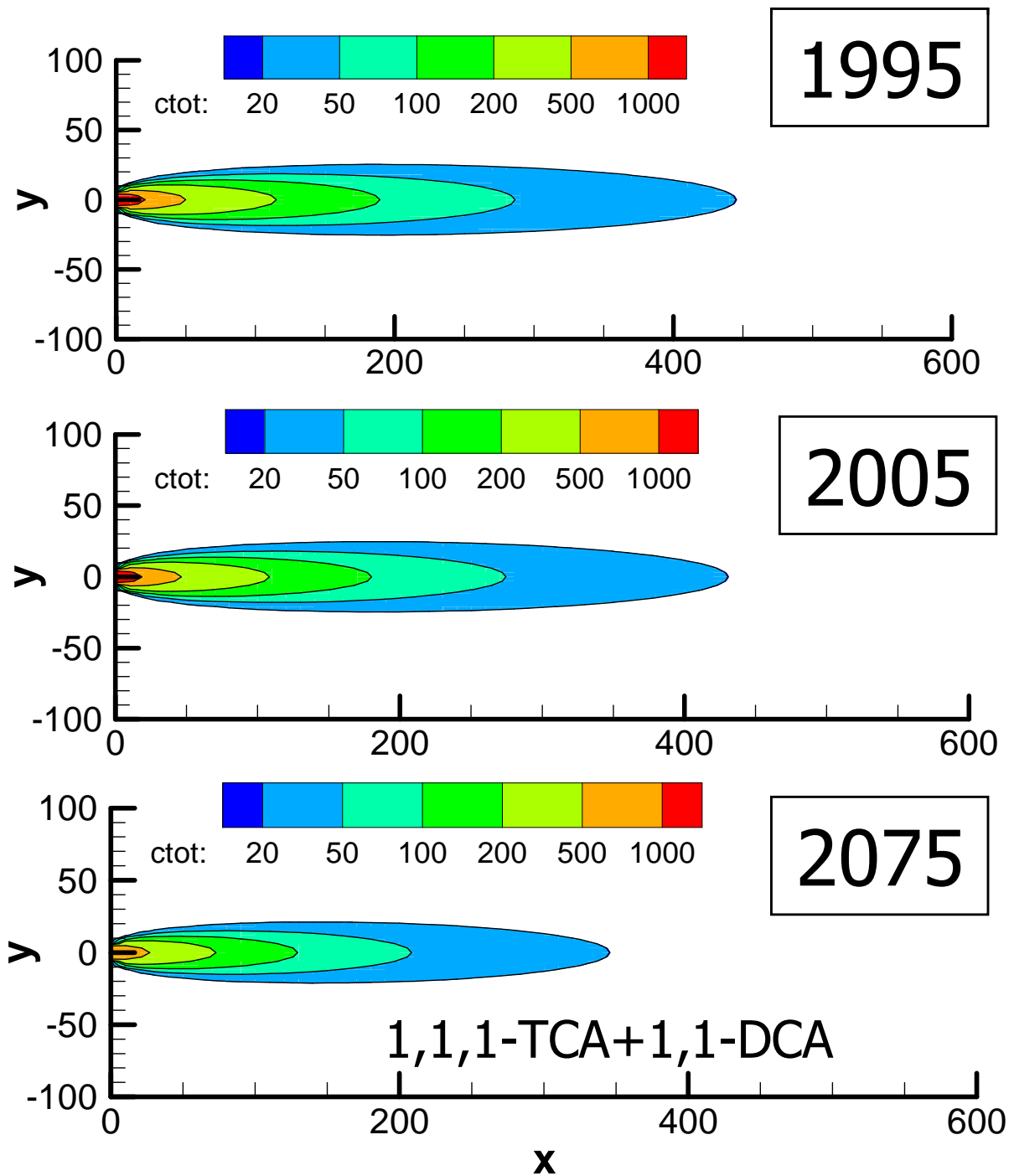
Another useful type of plot is one of plume discharge past different x locations. This is calculated in REMChlor, using the entire width and depth of the plume, so the discharge (technically it is not a “flux”) has units of kg of contaminant mass passing the x location per year. It is important to realize that transverse and vertical dispersion do not affect the flow direction discharge, because these mass fluxes are perpendicular to the flow direction, and they do not destroy any of the plume mass. Plume discharge plots are selected by choosing the “Mass Discharge” just below the graph. A formatted plot file (tutorial3_discharge.cfx) is provided, and the discharge at 30 years should look like this:

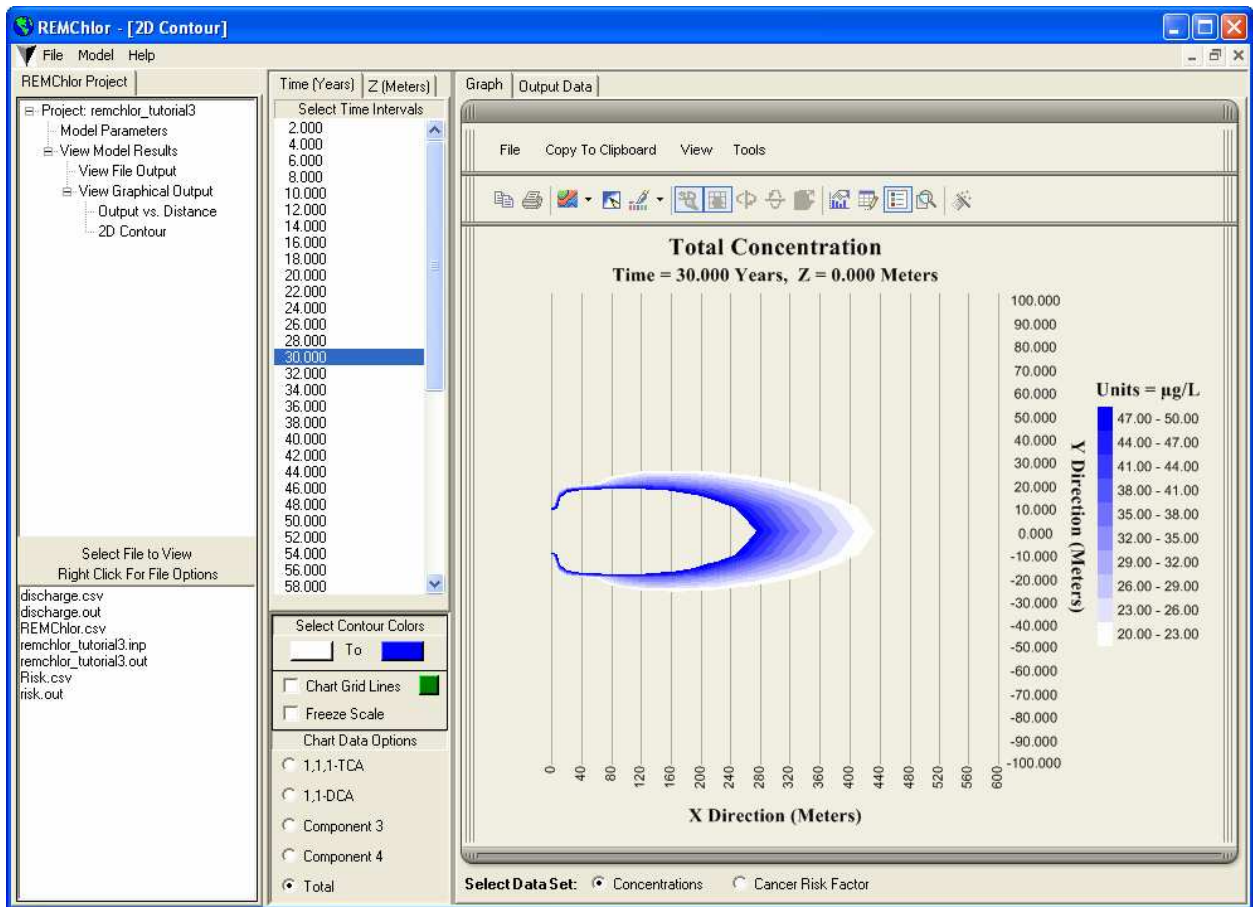


Two-dimensional contour plots can be produced from the graphical output created by REMChlor either within the program, or alternatively using an outside application such as TECPLOT™. The file REMChlor.csv gives a comma delimited output file with time, x,y,z, the 4 concentrations, and the total concentration. The project file with the .out extension has the same information in a space delimited TECPLOT™ format. This file also writes the input data, and reports on a few other calculations. These lines of the file would be deleted before loading into TECPLOT™. The figure on the next page shows the dissolved plume after 20, 30, and 100 years using TECPLOT™. The figure on the next page after that shows the REMChlor 2D Contour Map of the total plume after 30 years.

In the absence of any type of remediation, this spill would result in a plume that stabilizes at about 400 m, and very slowly shrinks with time. It is assumed for the purpose of this example that the outer extent of the plume is defined by a combined TCA+1,1-DCA contour of 20 ug/l. This plume is persistent, because the source is long-lived, and 30 years after the spill, 89% of the TCA mass remains in the source. The plume is limited in extent because the outer contour that defines the plume of 20 ug/l is only 100 times lower than the source concentration of 2 mg/l. Because this plume has a stable to slowly shrinking configuration, it could be a candidate for monitored natural attenuation. On the other hand, regulations or public pressure could require some actions to permanently reduce the size of the plume, for example to a maximum extent of 150 m. This could potentially be achieved through some combination of source

and plume remediation. These types of simulations are shown in the next two tutorial examples.

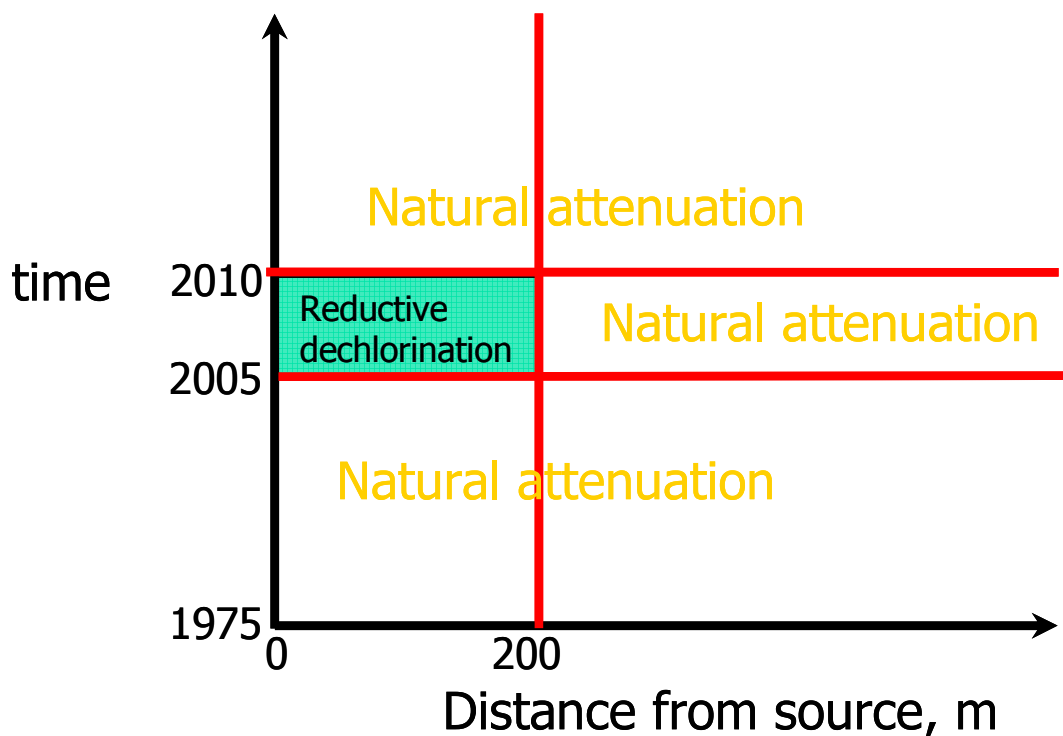




This contour map has been re-worked within REMChlor to depict only the 20 to 50 ug/L isopleths for the TCA/DCA plume at time = 30 years.

Tutorial 4: Natural Attenuation of a TCA DNAPL Source with Enhanced Plume Degradation

This tutorial example is identical to the previous natural attenuation case except that we will now consider enhanced biodegradation of the TCA and DCA in the dissolved plume. Here, the reductive dechlorination of TCA and DCA has been enhanced for the first 200 m over a 5 year period, from 2005 to 2010 (years 30 to 35), so that the TCA decay rate increases from 0.8/yr to 3.2/yr, and the DCA decay rate increases from 0.2/yr to 1.2/yr. This is illustrated graphically using a distance-time reaction zone plot (that corresponds to the REMChlor plume reaction matrix):

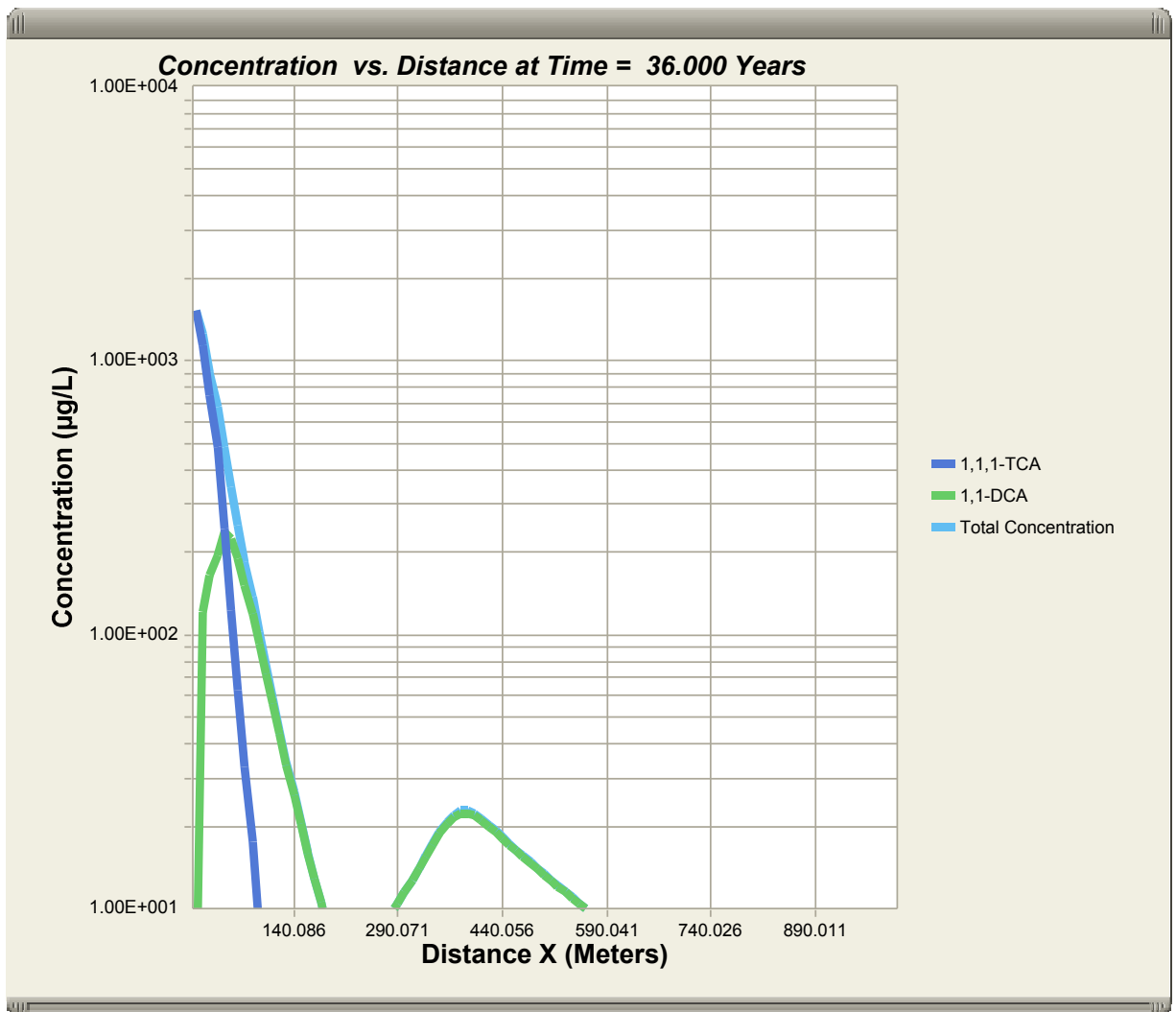


The enhanced degradation scheme shown above is implemented in REMChlor by first specifying the time-distance values for the reaction zones. The first time period (Period 1) ends as soon as the enhanced plume degradation begins, a time of 30 years. The second period (Period 2) ends when the enhanced degradation ends, after 35 years. The first zone extends from the DNAPL source, to a downgradient distance (X1) of 200 m. An additional zone could be specified, but it is not needed here.

The different plume decay rates as a function of space and time are entered into REMChlor for each component using the matrix that is analogous to the figure above.

The enhanced degradation rates would reflect a good rate of plume attenuation (Aziz et al., 2002), and this type of enhancement could possibly be achieved through the addition of an electron donor (Wiedemeier et al., 1999; Aziz et al.,

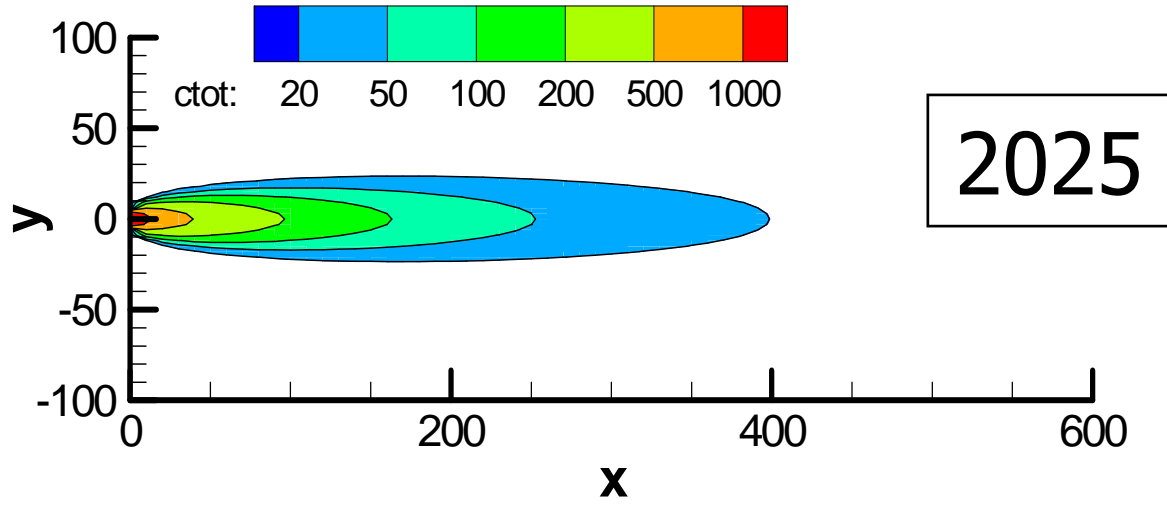
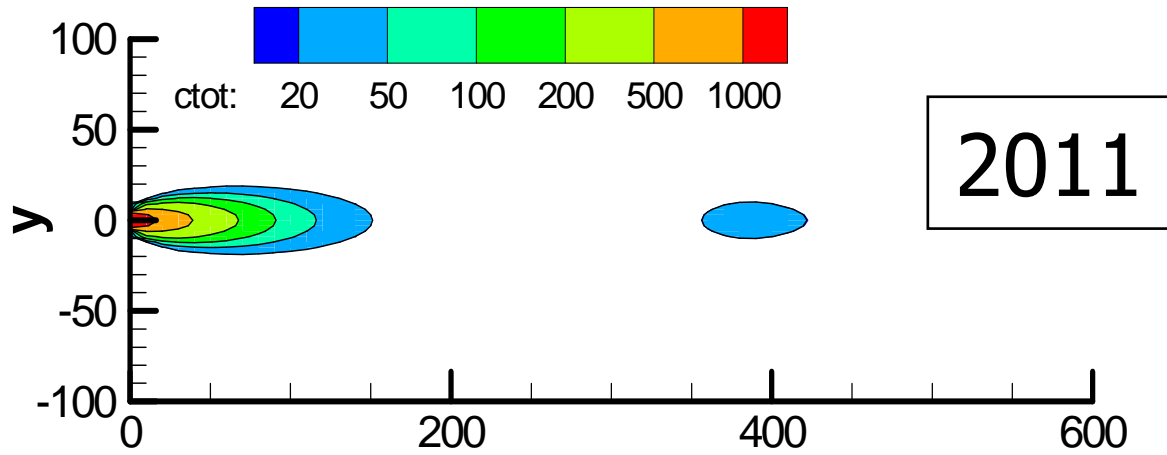
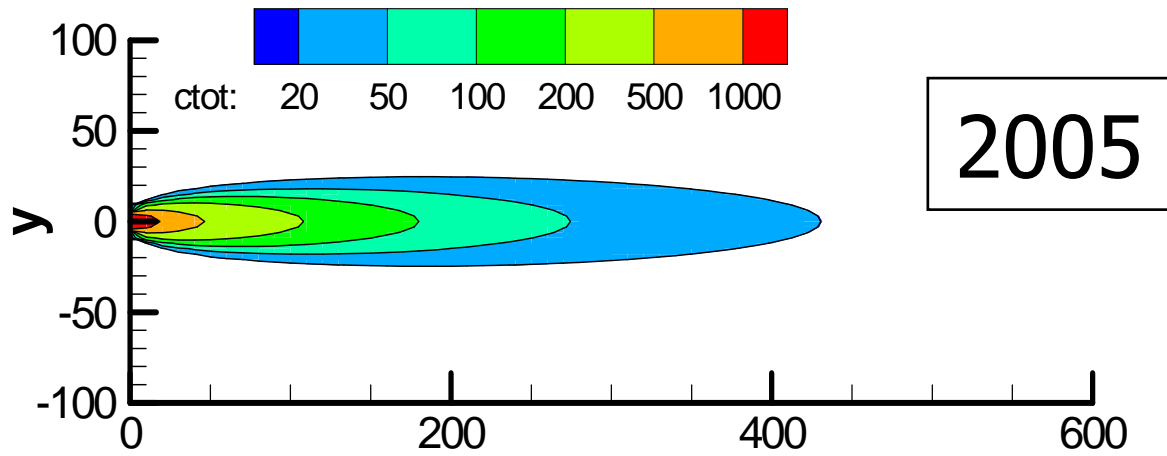
2000; Alvarez and Illman, 2006). Using the provided tutorial4.cfx file, the concentration profile at 36 years should look like this:



A formatted mass discharge plot file is also included in this folder (tutorial4_discharge.cfx).

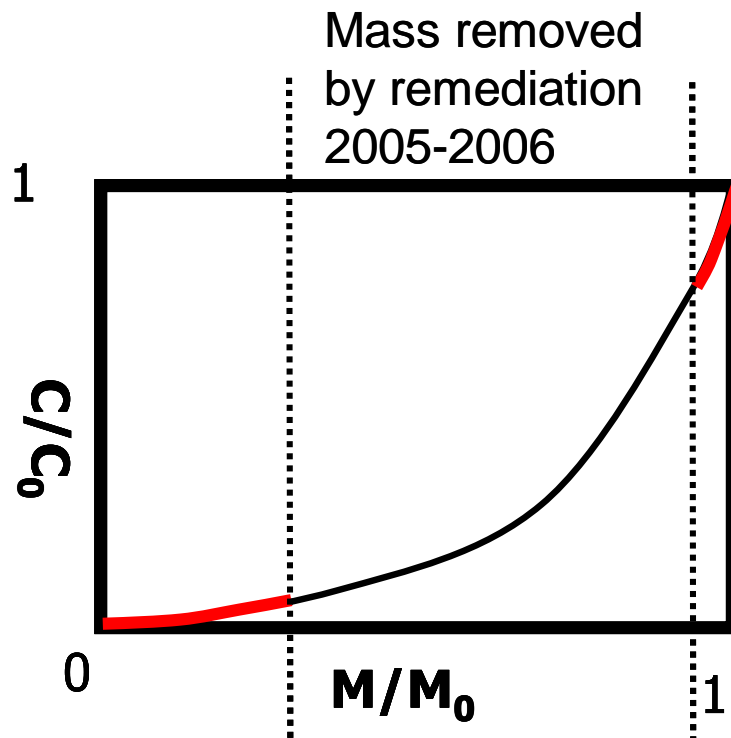
The plume remediation effort is clearly effective in reducing the plume size as long as it is active. However, as shown on the next page, once the treatment ends, the plume rebounds to nearly its original size. If the plume treatment were continued indefinitely, the plume would remain small, however.

Again, these contour plots can be constructed within the REMChlor application. TECPLOT™ was used for the figure here.



Tutorial 5: TCA Source Remediation with Natural Attenuation of the Plume

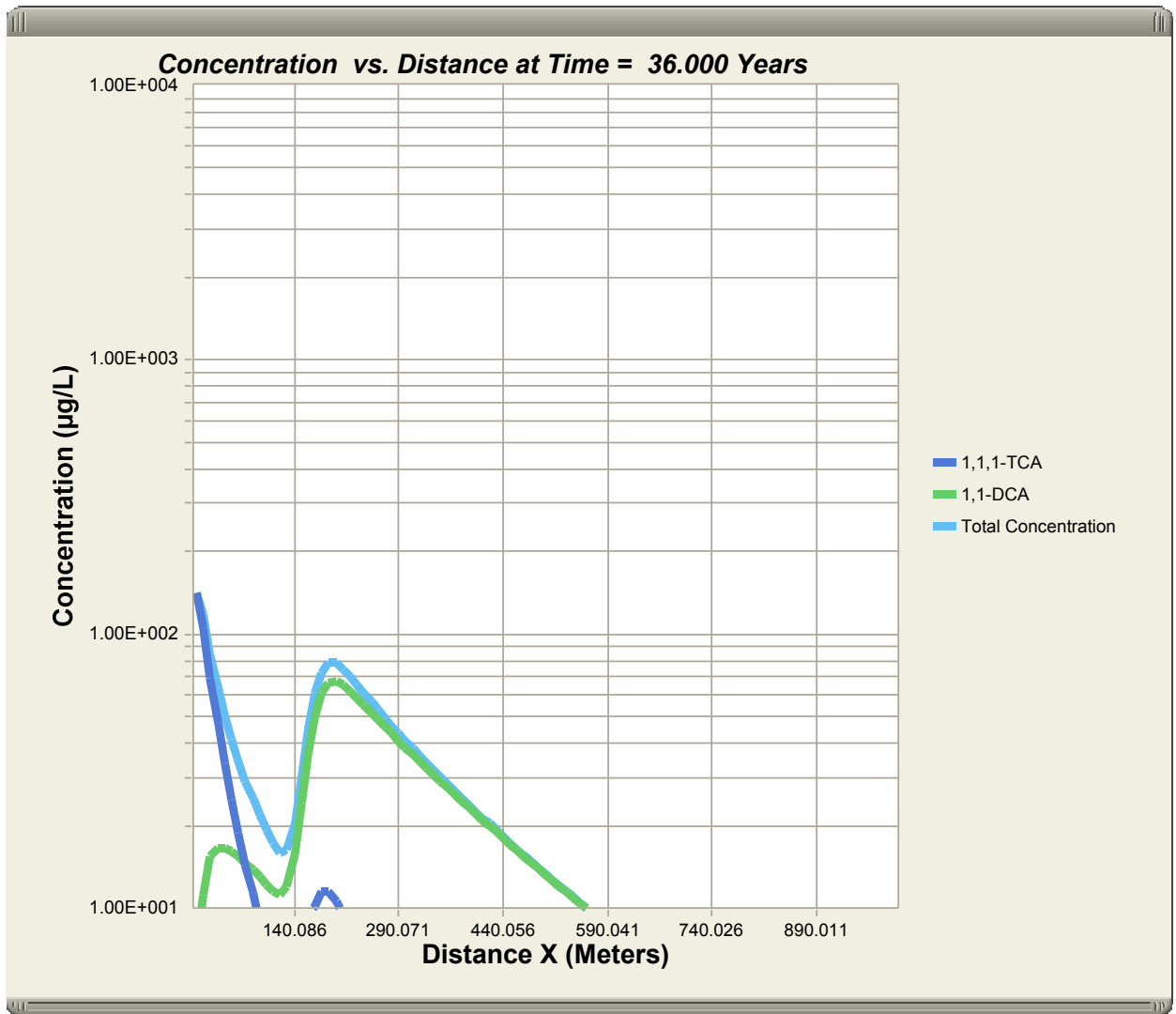
This tutorial example is identical to Tutorial 3, except that a partial DNAPL source remediation effort is modeled. This remediation could consist of excavation, or some type of in-situ remediation (air sparging, steam flooding, alcohol or surfactant flooding, for example). A reasonable source remediation goal would be the removal of 70% of the source mass. With the source model given by Equation (2) with an exponent (Γ) of two, removal of 70% of the source mass leads to a reduction in the source discharge of 91%. For this example, we will assume that the source remediation takes place between 2005 and 2006 (years 30 and 31). The source mass/source concentration plot for this case is shown below:



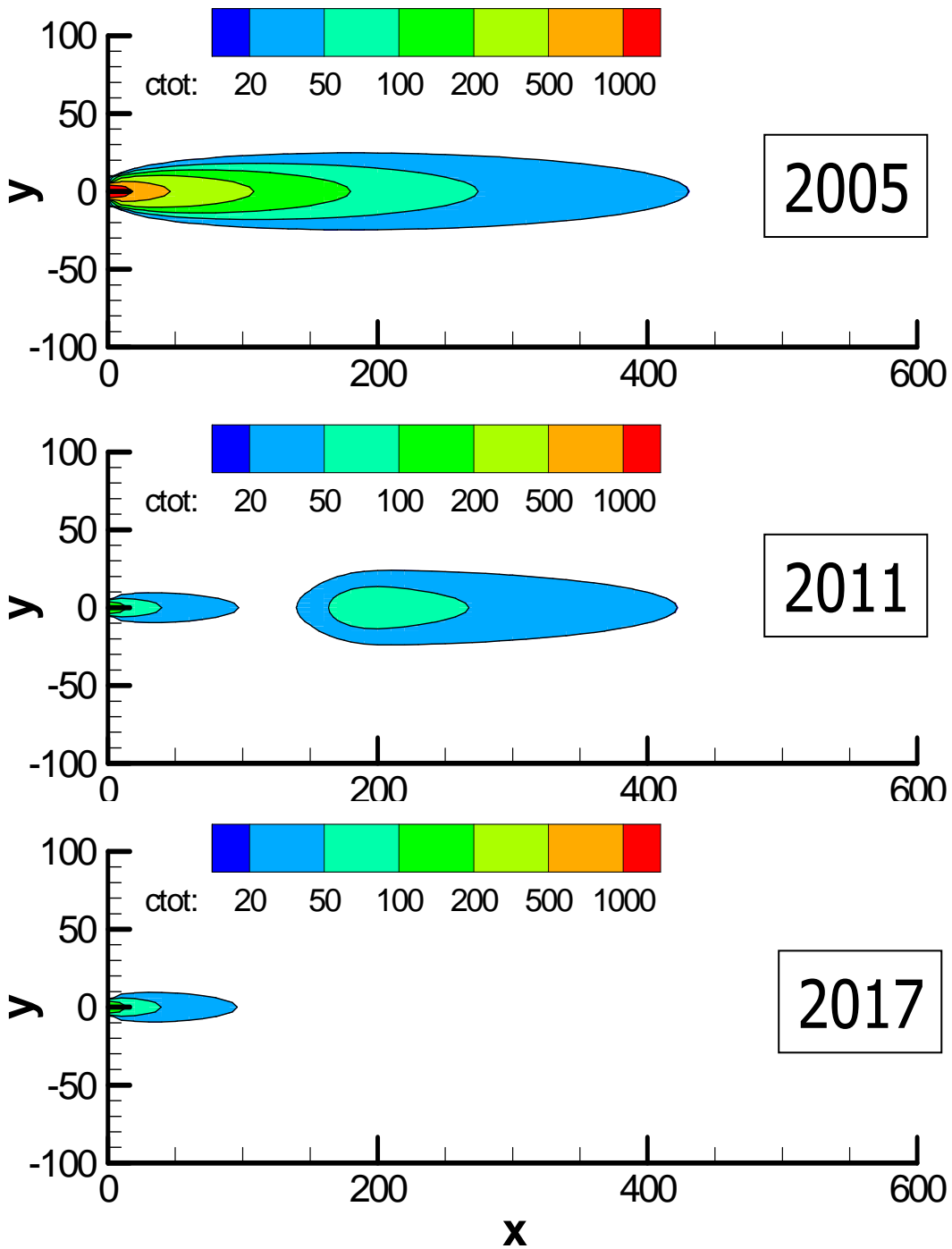
The plume discharge initially has a value of C_0 , at the upper right-hand corner of the graph. Over the first 30 years, the TCA source dissolves into the plume, so the source mass and discharge are slowly reduced. The source remediation in 2005-2006 removes 70% of the DNAPL mass, so the source mass and discharge jumps to the new location on the curve, where it remains for the rest of the simulation. During this later time, the source continues to be depleted by dissolution.

The source remediation in REMChlor was specified by choosing a value of 0.7 for the “Percent Removed Fraction” variable, a remediation start time (T1) of 30 years, and a remediation end time (T2) of 31 years. REMChlor assumes a linear removal of the source during this specified remediation period. A centerline

plot of the plume concentration at 36 years (using the tutorial5.cfx format) should look like this:



Once the source is reduced, the plume splits into two parts, because no effort was made here to treat the plume. As shown in the contour plots on the next page, after a few years, the downstream part of the plume decays away, leaving only a small plume located near the source. This small plume then remains stable and slowly shrinks over the next 100 years or so.



This example is representative of a site that is fairly manageable. Although the source is potentially long-lived, the ground water velocity is high, and the rate of natural attenuation is low, the ratio of source concentration (2 mg/l) to the acceptable regulatory concentration (assumed to be 20 ug/l) is only 100. This site could be much more difficult to manage if this ratio was a few orders of magnitude larger, as is the case in the next example.

Tutorial 6: Natural Attenuation of a PCE DNAPL Source and Dissolved Plume

This example involves a hypothetical 1975 release of 1620 kg of PCE DNAPL into an aquifer with a groundwater darcy velocity of 10 m/yr, and a porosity of 0.333. The source has dimensions of $Y=10$ m and $Z=3$ m so the total flowrate through the source zone is 300 m³ per year. The source is assumed to behave according to Equation (2), with an exponent, Γ , of 1. This type of source behavior gives an exponential decay of the source mass and concentration with time (Newell et al., 1996; Parker and Park, 2004; Zhu and Sykes, 2004; Newell and Adamson, 2005). The initial source concentration (C_0) was 100 mg/l, leading to large initial source discharge of 30 kg of PCE per year.

Under natural plume conditions, it is assumed that the PCE undergoes reductive dechlorination to TCE and then DCE. It is further assumed that the 50% of any DCE that is degraded is converted to VC by reductive dechlorination, but the remaining 50% is destroyed in other reactions that do not produce VC. This change in the production of daughter product is simulated by reducing the DCE to VC yield coefficient by 50%. The background chlorinated ethylene degradation rate coefficients of PCE=0.4/yr, TCE=0.15/yr, DCE= 0.1/yr, and VC=0.2/yr would be representative of site conditions where the rate of degradation is low, and natural attenuation is weak (Wiedemeier et al., 1999; Aziz et al., 2002).

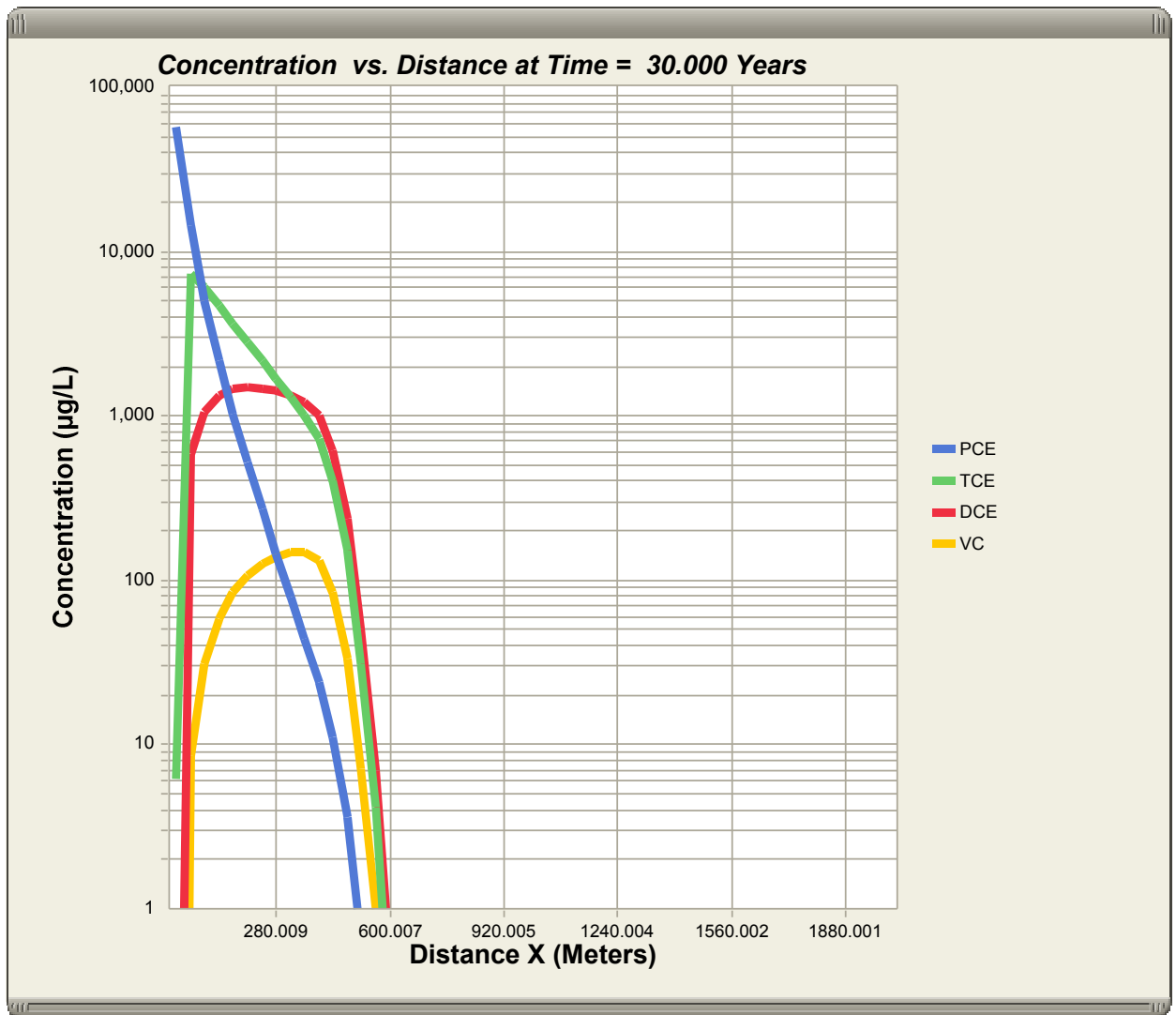
The compounds were assigned a retardation factor of 2, the longitudinal dispersivity is equal to 0.005 times the travel distance, the transverse dispersivity is 0.5 m, and the vertical dispersivity is 0.1m. PCE, TCE, and VC are considered to be carcinogens, and the cancer risks are calculated using the methods described earlier, with the California cancer risk slope factors (OEHHA, 2006) shown below:

Chemical	Inhalation Slope Factor (mg/kg-day) ⁻¹	Oral Slope Factor (mg/kg-day) ⁻¹
Tetrachloroethylene (PCE)	0.021	0.540
Trichloroethylene (TCE)	0.007	0.013
Cis-1,2-Dichloroethylene (DCE)	-not a carcinogen	-not a carcinogen
Vinyl chloride (VC)	.270	0.270

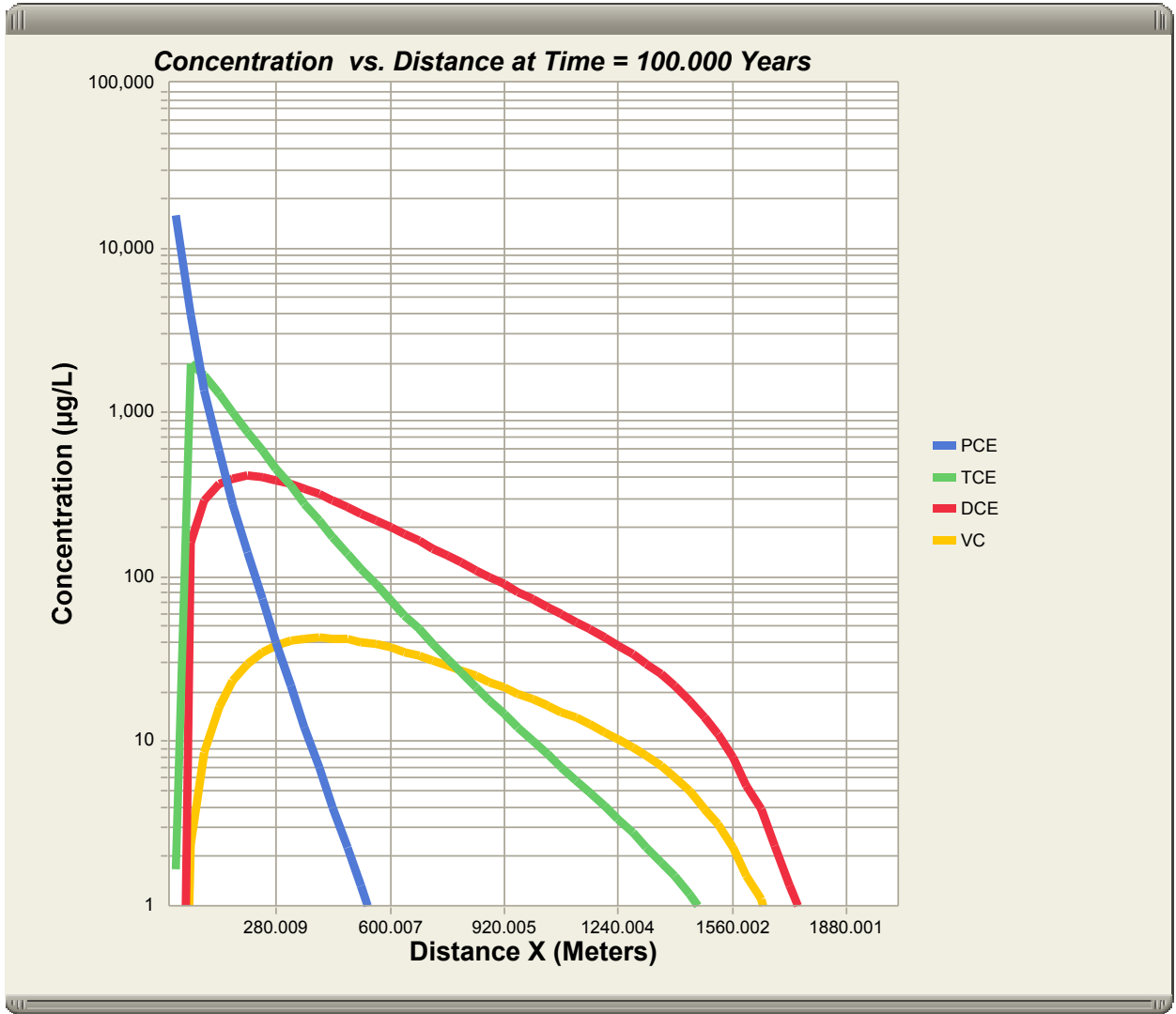
The federal drinking water standards for PCE, TCE, DCE and VC are 5, 5, 70, and 2 ug/l, respectively.

The REMChlor input for this problem is similar to the TCA natural attenuation example (Tutorial 3), except that this problem involves more daughter products, and the cancer risk calculations are important. Running the problem, and using

the formatted concentration plot file (tutorial6.cfx), the concentration profile along the plume centerline at 30 years should look like this:

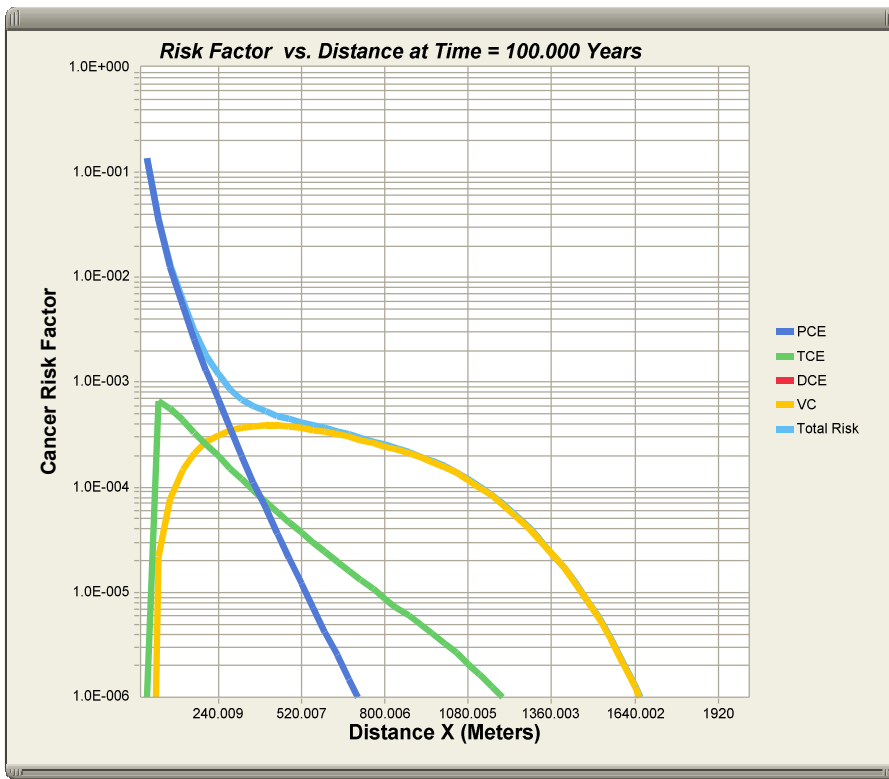
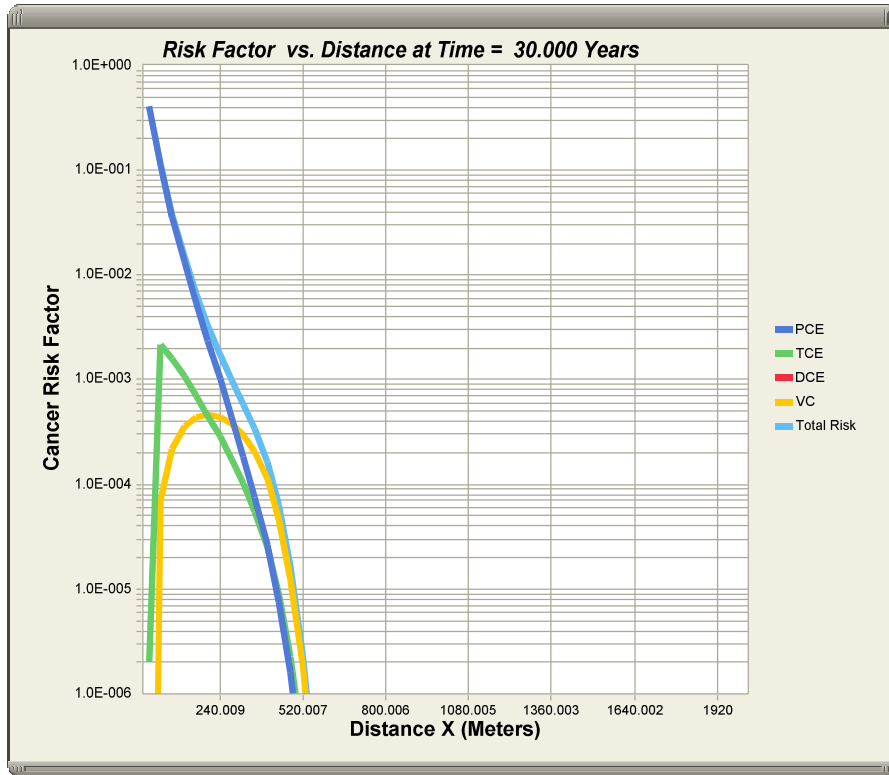


In the absence of any type of site remediation, this release would result in a large plume that would not stabilize for more than 100 years. This can clearly be seen by plotting the centerline concentrations at 100 years:



At earlier times, and at locations near the release, the plume is dominated by PCE and TCE. At later times, and at distances that are further from the source, DCE and VC predominate. The plume continues to grow in this example, even as the source is being depleted by dissolution. After 30 years (2005), about 57% of the PCE DNAPL remains in the source zone, and the dissolved plume is 550 m long. At 60 years (2035), the plume is about 1100 m long, and 33% of the source remains, and at 100 years (2075), the plume is about 1600 m long and 15% of the source remains.

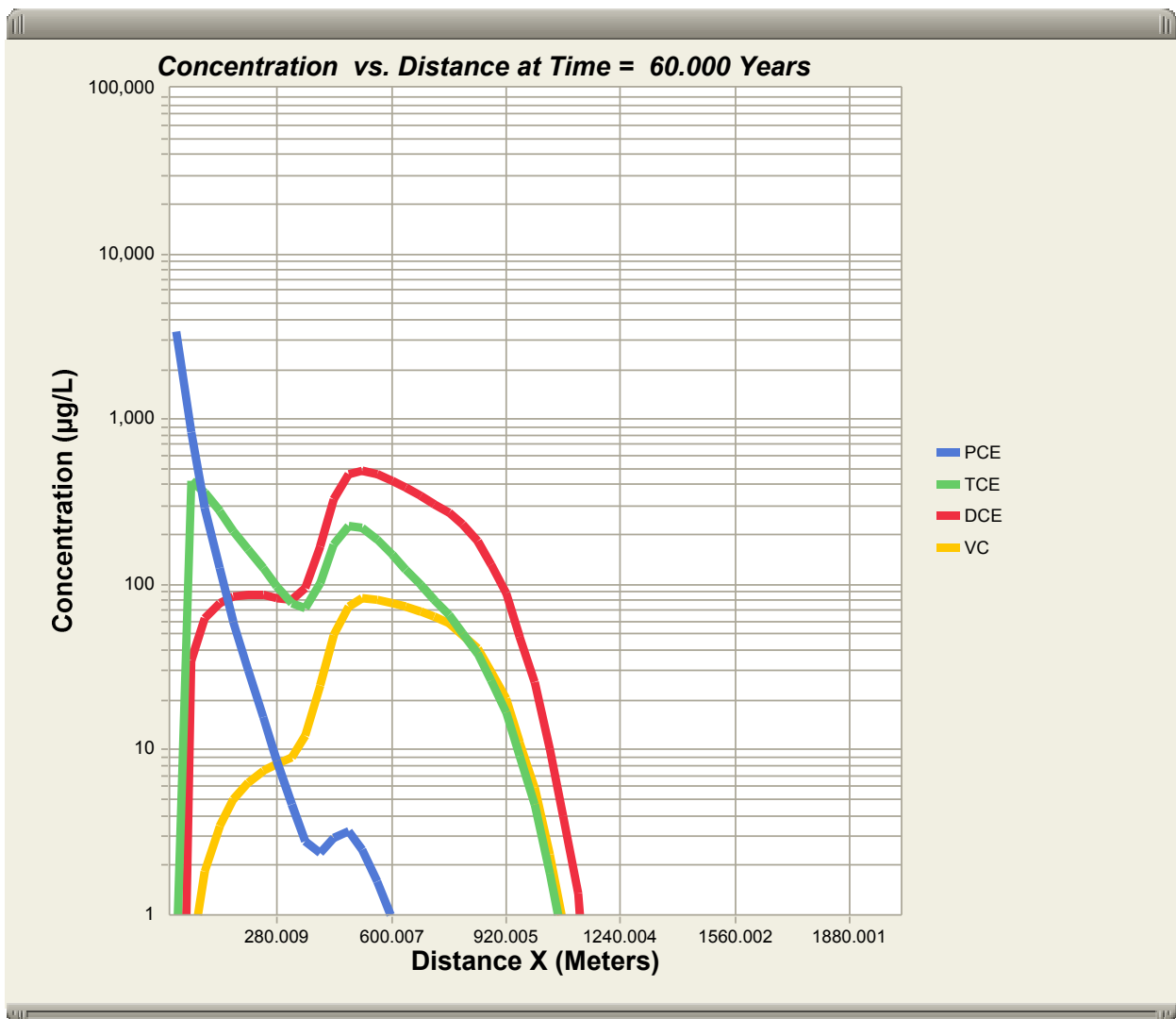
The theoretical cancer risks that would result from contaminated well water are shown can be plotted by selecting the Cancer Risk Factor button below the graph. A formatted plotting file for the risk graph is included (tutorial6_risk.cfx). The cancer risks posed by the plume (along the centerline) at 30 and 100 years should look like these:



These risks are based on ingestion of contaminated water, and inhalation of vapors coming from the water in the house. The ingestion and inhalation exposure parameters were given earlier in the analytical model description section. The risk shown here does not include any contribution from direct vapor transport from the plume through the vadose zone into the house, and in some cases this could provide a substantial exposure route as well (Johnson and Ettinger, 1991; Johnson et al. 2002). The risk near the source is very high, and is dominated by the PCE, due to its high concentration and its high oral slope factor (using the California value). Downgradient from the source, the risk becomes dominated by the vinyl chloride due to its significant concentration and its high oral and inhalation slope factors. This becomes especially true at large times. One hundred years after the release, the lifetime cancer risk remains very high near the source, and it exceeds a value of 10^{-5} for a distance of more than 1400 m.

Tutorial 7: PCE Source Remediation with Natural Attenuation of the Plume

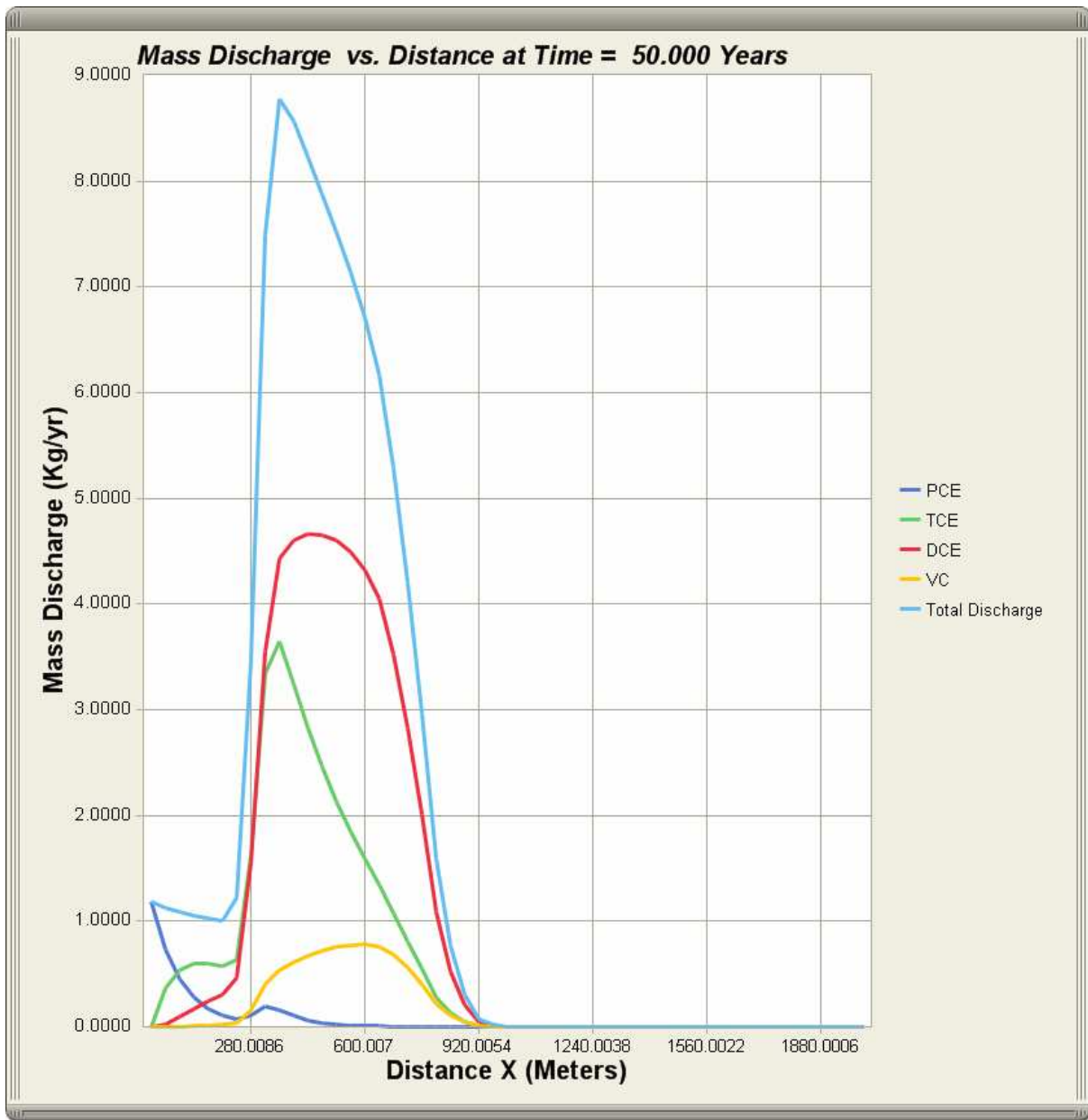
This example is exactly like the previous tutorial except that it considers partial source remediation. Using the source model, Equation (2), with an exponent (Γ) of one, the removal of some fraction of the source mass results in an equal reduction in the source discharge. Therefore, a source remediation effort that removes 90% of the source would be expected to reduce the downgradient concentrations by a factor of 10. This REMChlor input page models a 90% removal of the remaining PCE source between 2005 and 2006 (years 30 to 31). Running the problem, and using the provided plotting format file (tutorial7.cfx), the plume centerline concentrations at 60 and 100 years should look like the graphs below:





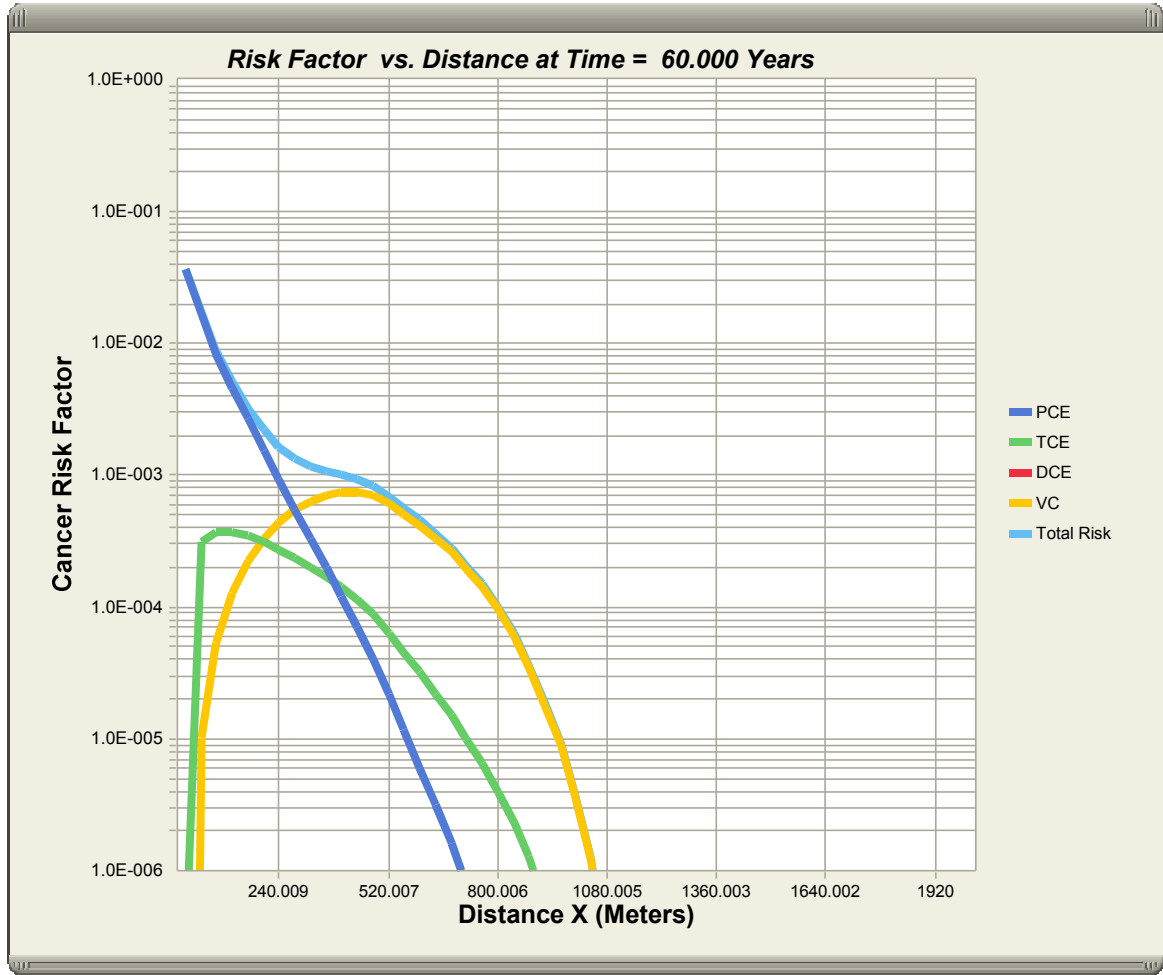
Thirty years after the source remediation (sixty years total), the dissolved concentrations between $x=0$ and about 400 m show a tenfold reduction. However, ahead of about 500m, the plume is essentially identical to the case shown previously, where there was no remediation. This occurs of course, because much of the contaminant mass was already in the plume when the source remediation was performed. A similar effect is seen 70 years after source remediation (one-hundred years total), where the concentrations at distances less than about 1000 m show a tenfold decrease in concentration, while the concentrations beyond about 1200 m are the same as the no-remediation base case.

The plume discharge shows a similar pattern of reduction. Using the included discharge plotting format file (tutorial7_discharge.cfx), the plume mass discharge at 50 years (20 years after source remediation looks like:



This plot used a regular y-axis scale, which shows the order of magnitude reduction in plume discharge that results from the source remediation.

The cancer risk along the plume centerline, using the formatted plot file (tutorial7_risk.cfx) is shown below:



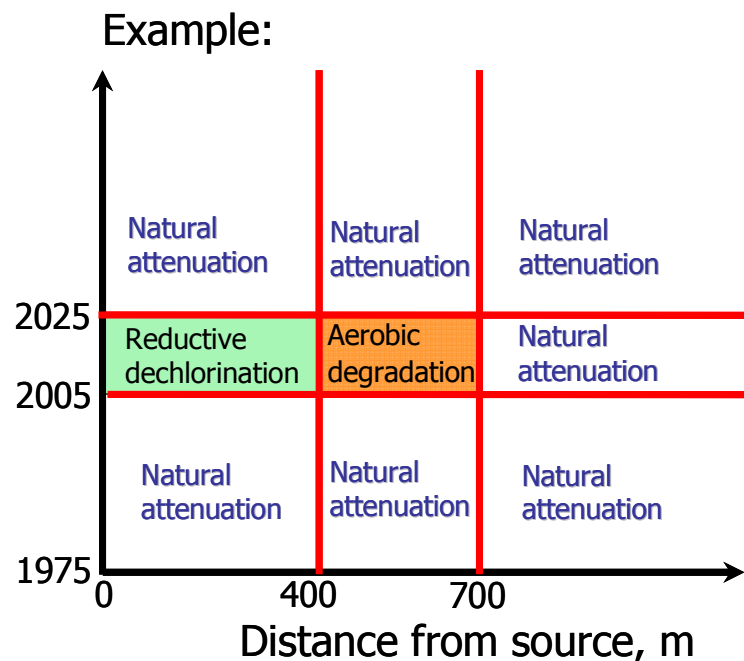
Thirty years after the start of remediation (2035, a total time of 60 years), the risk reduction due to source remediation alone is less than a factor of 10, with most of the reduction occurring near the source. The risk reduction in that case decreases with increasing distance because a 30 year exposure period is used (2005-2035), and downgradient concentrations are not immediately affected by source remediation. The downgradient risks are reduced more substantially with the addition of plume remediation, which is shown in the next example.

Tutorial 8: PCE Source Remediation with 2 Zone Enhanced Plume Degradation Design

This final example builds on the previous tutorial, and it adds plume remediation to the source remediation. In the case of PCE and its daughter products, it is known that PCE and TCE degradation may be enhanced through the addition of electron donors such as hydrogen, lactate, or molasses that act to increase reductive dechlorination (Weidemeier et al., 1999; Alvarez and Illman, 2006). Depending on the site conditions though, it is possible that this treatment may not proceed through DCE and VC to ethylene, since they are somewhat less effectively degraded by the reductive dechlorination mechanism (Weidemeier et al., 1999; NRC, 2000; Alvarez and Illman, 2006). When this happens, the process is said to “stall” at DCE, and this behavior has been observed at several field sites (McGuire et al., 2004). One strategy that could be used in this situation would be to create an enhanced aerobic degradation zone downgradient from the reductive dechlorination zone. This might be done through air sparging, or the injection of oxygen, ozone, H_2O_2 , or some other oxygen releasing compound. This zone would then favor the aerobic degradation of DCE and VC, although it would probably not further degrade any PCE or TCE present (NRC, 2000; Weidemeier et al., 1999; Alvarez and Illman, 2006).

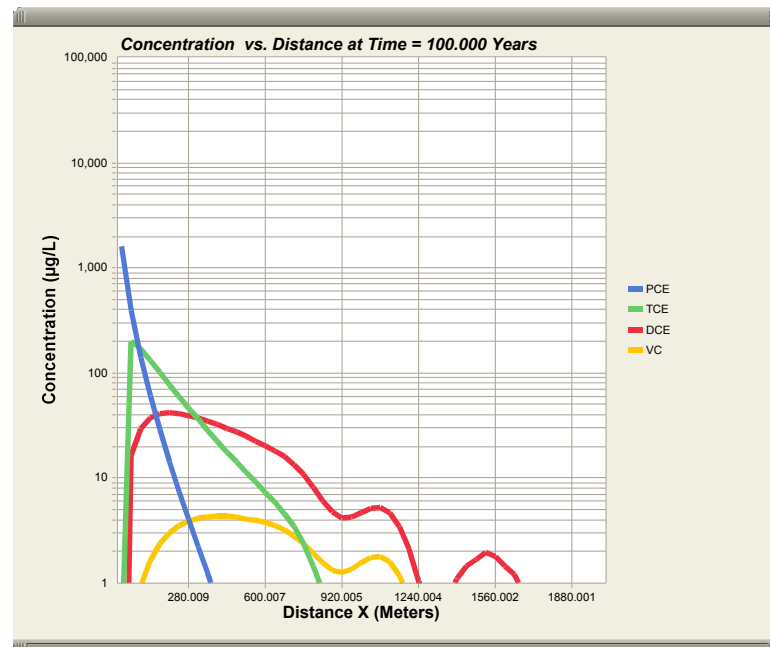
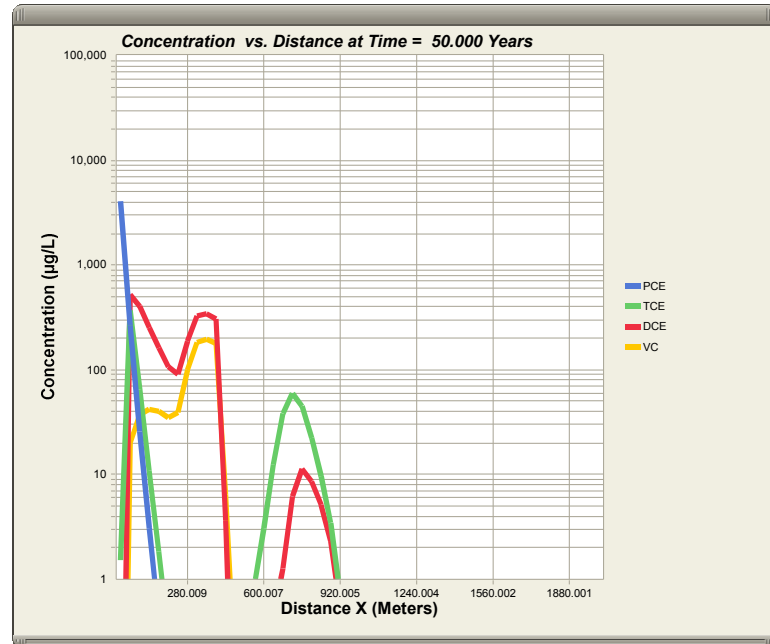
The effects of a two-zone plume remediation effort was simulated using the decay rates shown below.

Plume reaction type	k_{PCE} , 1/yr	k_{TCE} , 1/yr	k_{DCE} , 1/yr	k_{VC} , 1/yr
Natural Attenuation reaction zones	0.4	0.15	0.1	0.2
Enhanced Reductive Dechlorination, reaction zone	1.4	1.5	0.2	0.2
Enhanced Aerobic Degradation, reaction zone	0.4	0.15	3.5	3.6



The enhanced plume remediation begins at the same time as the source remediation, 2005, and it continues until 2025. The reductive dechlorination zone is active for the first 400 m, and it works to rapidly degrade PCE and TCE, but not DCE or VC. The aerobic degradation zone extends from 400 to 700 m, and it rapidly degrades the PCE and VC, but not PCE or TCE. These zones in space and time were defined in the REMChlor plume decay window, and the rates for each of the 4 components must be included.

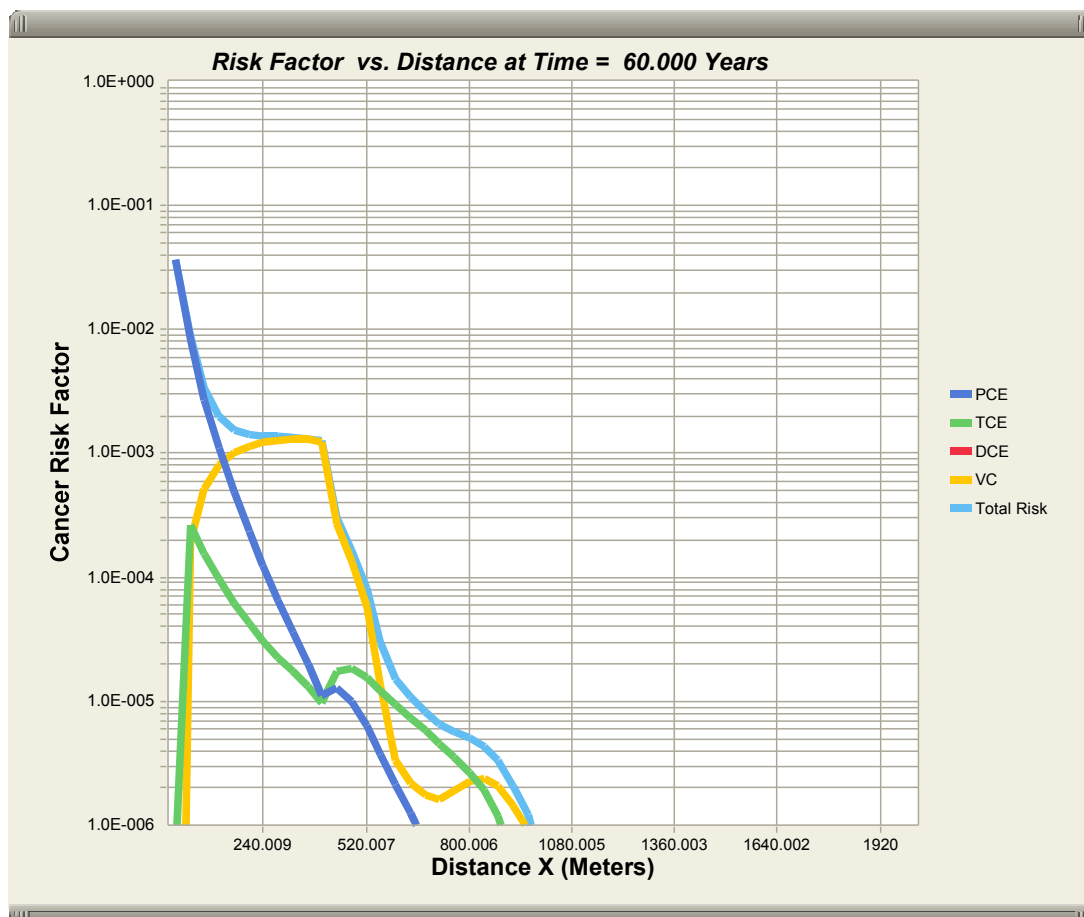
The the centerline concentrations resulting from this combined effort are after 50 and 100 years (years 2025 and 2075) should look like this:

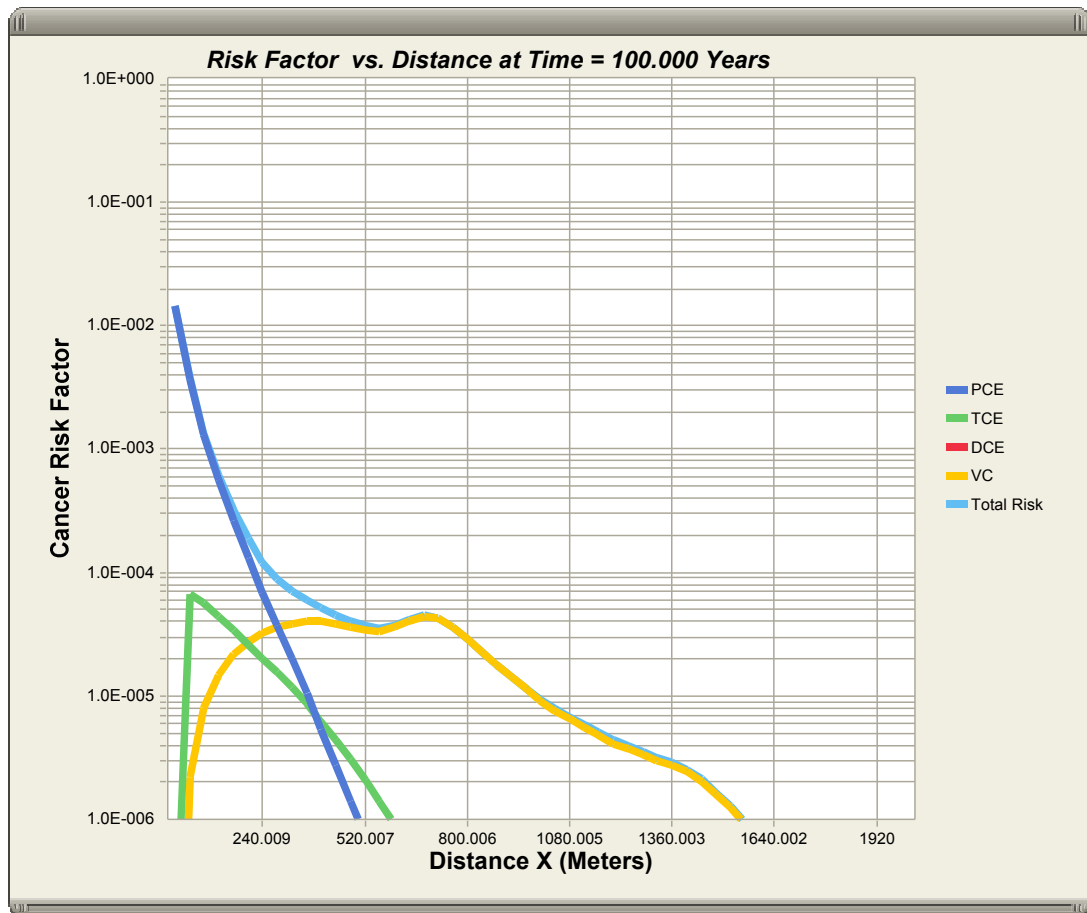


Immediately following the plume treatment (2025), the effects of the different reaction zones are clearly seen. Both the PCE and TCE concentrations drop very rapidly over the first 200 m due to their increased decay rates. The DCE and VC, however increase in this zone because they were assumed not to degrade effectively under the strong reducing conditions present in this zone. The DCE and VC concentrations drop very quickly in the downgradient reaction zone, which begins at $x=400$ m. A small amount of TCE and DCE are located beyond the end of this aerobic treatment zone, due to the fact that this TCE was already out of the reductive dehalogenation zone when the plume treatment started in 2005.

The plume begins to rebound some following the plume treatment, but the concentrations are consistently lower throughout the plume than they were in the case without remediation. Seventy years after the start of remediation (a total time of 100 years), the first 700 m of the plume takes on the configuration of the previous case with only source remediation. This happens because the part of the plume that was treated from 2005 to 2025 has been carried an average of 750 m downgradient by advection. Ahead of this location, the plume concentrations are much lower than they were in the case with source remediation alone.

The effects of the source and plume remediation on cancer risk in 2035 and 2075 (60 and 100 years total time) are shown below, using the formatted plot file (tutorial8_risk.cfx).





Seventy years after the start of remediation (year 2075, 100 years total), the cancer risks (for an exposure period of 2045-2075) are an order of magnitude or more lower throughout the plume for the case of combined source and plume remediation. Whether this would be an acceptable risk for uncontrolled use of this water would depend on what risk was considered acceptable. If the acceptable lifetime cancer risk was 10^{-4} , then the remediation effort would in effect reduce the plume from a length of 1200 m to a length of 250 m. In other words, with the combined remediation scheme, a household using well water beginning in 2045 from $x > 250$ m would never experience an excess cancer risk greater than 10^{-4} , whereas that minimum distance would be 1200 m without any remediation.

These PCE examples are much more difficult to manage than the earlier TCA cases for several reasons. First, the source concentration was very high compared to allowable regulatory levels, a ratio of 20,000:1. Second, the source discharge was high relative to the natural attenuation rate, so the plume did not stabilize in a reasonable time-frame. Finally, the decay reaction produced daughter products that were as hazardous or even more hazardous than the parent compounds. Sites with these characteristics are likely to require either perpetual plume remediation, or else some combination of source and plume remediation.

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