# REMFuel

## Remediation Evaluation Model for Fuel Hydrocarbons

## User's Manual
## Version 1.0

**by**

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# Overview

## Abstract

An analytical solution, called **REMFuel** (for **R**emediation **E**valuation **M**odel for **Fuel** hydrocarbons) has been developed for simulating the transient effects of groundwater source and plume remediation for fuel hydrocarbons. In the analytical method, the contaminant source model is based on a power function relationship between source mass and source discharge for multiple fuel constituents, 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 for each fuel component simulates first order sequential decay and production of one daughter species. **REMFuel** can also simulate zero order or Monod's kinetics for decay of fuel components in the plume. The decay rates and other reaction coefficients are variable functions of time and distance in the plume. This approach allows for flexible simulation of enhanced plume remediation that may be temporary in time, limited in space, and which may have different effects on different contaminant species in the plume.

The Center for Subsurface Modeling Support (CSMoS) at EPA has developed a Graphical User Interface (GUI), for **REMFuel** that will allow the user to quickly and easily evaluate the balance of LNAPL 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 **REMFuel** 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.

**REMFuel** provides a suite of powerful tools for building and interpreting models.

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# REMFuel Software Installation and Computer Requirements

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1. To install the software, run the file ‘REMFuelsetup.exe’. The software will guide the user through the installation process. Upon first running this beta version of REMFuel from the desktop icon, the user will be asked to run it again. This serves to initialize the application after which REMFuel will run properly in Windows.
2. REMFuel v 1.0 requires a standard PC running Windows 98 or greater. The .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 fuel hydrocarbons (BTEX and other gasoline additives) at thousands of sites from gasoline spills. Many of these sites contain light nonaqueous phase liquids (LNAPLs) that serve as a concentrated source of groundwater contamination, and most dissolved plumes of volatile organic chemicals (VOCs) can be traced back to concentrated source zones. The VOCs often are suspected 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 VOC plumes is a realistic goal that can be achieved through various combinations of source and plume remediation.

The Center for Subsurface Modeling Support (CSMoS), a unit of EPA’s Ground Water and Ecosystem Restoration Division (GWERD), distributes a modeling software package called REMChlor (**R**emediation **E**valuation **M**odel for **Chlor**inated solvents that simulates the transient effect of groundwater source and plume remediation for chlorinated solvents [Falta, 2008]. In this project, similar modeling software, named REMFuel (**R**emediation **E**valuation **M**odel for **Fuel** hydrocarbons) has been developed for gasoline and other fuel components. Similar to REMChlor, REMFuel assumes a power function relationship between source mass and source discharge, and it can consider partial source remediation at any time after initial release. The contaminant source is composed of multiple fuel constituents, and can be depleted naturally by the processes of dissolution and first order aqueous phase 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. Also similar to REMChlor, the plume model in REMFuel simulates first order sequential decay and the production of daughter species; however, it only considers production and decay of one daughter product from sequential decay. Allowing only one daughter product seems sufficient for gasoline and other fuel components. Additional features in REMFuel include zero order decay and Monod’s kinetics options in the plume model. 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, and they are independent for each fuel species in the plume. This approach allows for flexible simulation of enhanced plume degradation that may be temporary in time and limited in space.

# LNAPL Source Model in REMFuel

The LNAPL source model in REMFuel is similar to that in REMChlor except that it considers biodecay in the aqueous phase only [Parker and Falta, 2008], and it considers multiple source zone contaminants. The contaminant discharge for each component from a source zone is the product of the flow rate of water passing through the source zone and the average concentration of contaminant in the water (Figure 1). Source discharge has units of mass per time, and should not be confused with mass flux, which is discharge divided by area. If water flows through the source at a rate of *Q(t)*, and if the mass in the source zone is also subjected to first order aqueous phase decay, then a mass balance on the source gives:

$$\frac{dM(t)}{dt} = -Q(t)C_s(t) - \phi\forall\lambda_s C_s(t) \qquad (1)$$

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

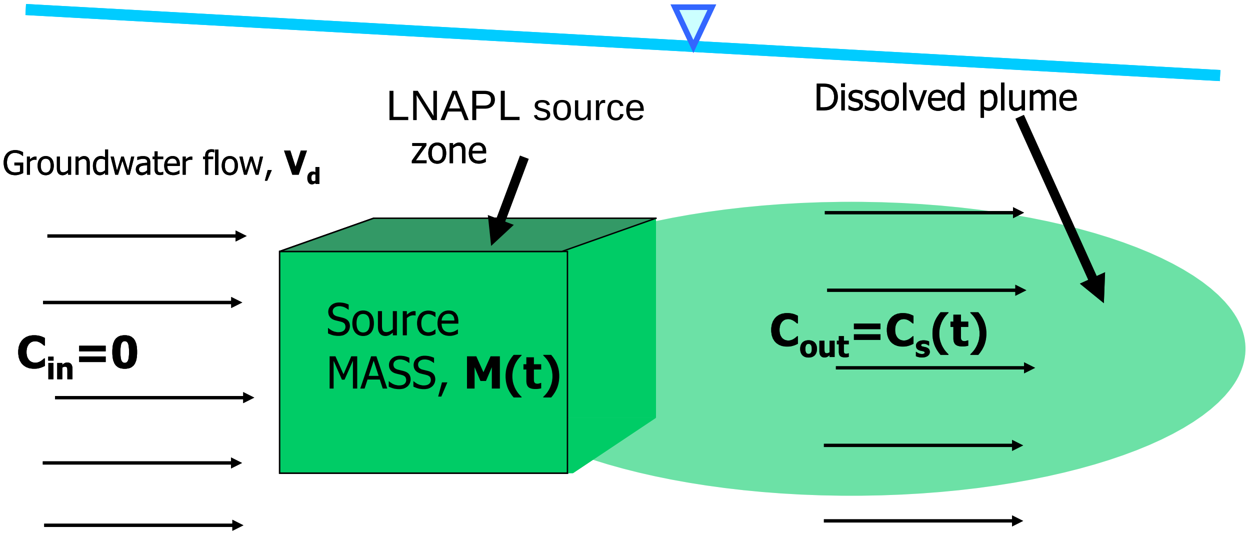


**Figure 1. Conceptual model of source zone with time-dependent contaminant mass and discharge.**

The source mass/source discharge relationship is shown in Figure 2, and it is modeled 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):

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

where $C_0$ is the flow-averaged source concentration corresponding to the initial source mass, $M_0$. The exponent, $\Gamma$, determines the shape of the source discharge response to changing source mass (Figure 2).

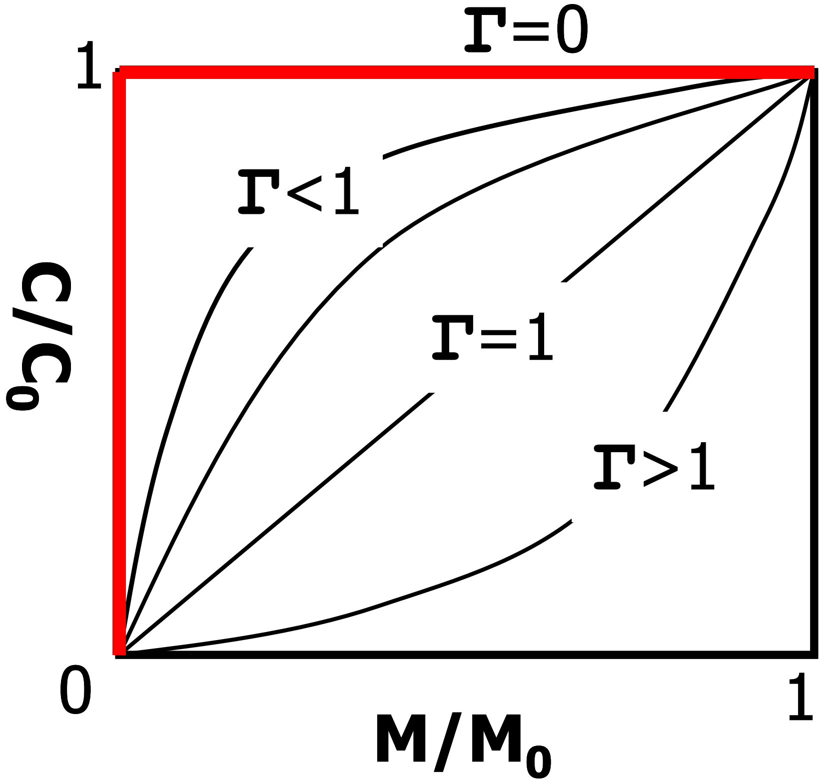


**Figure 2. Power function representation of source mass/source discharge relationship (Equation 2)**

Field, laboratory, and theoretical evaluations of the source mass/source discharge response suggest that $\Gamma$ may vary between about 0.5 and 2 at real sites [Rao and Jawitz, 2003; Falta et al., 2005a; Newell and Adamson, 2005; Fure et al., 2005; Jawitz et al., 2005; McGuire et al., 2006; Newell et al., 2006]. Simulation studies suggest that sites with DNAPL located predominantly in low permeability zones exhibit $\Gamma > 1$ and sites with DNAPL in high permeability zones exhibit $\Gamma < 1$ [Falta et al., 2005 a, b]. Park and Parker [2005] suggest $\Gamma$ values greater than 1 for finger-dominated residual DNAPL and less than 1 for DNAPL pools. Essentially, $\Gamma$ should be considered as an uncertain parameter, whose mean value can be roughly estimated, but whose actual value may never be precisely known at a site.

Equations (1) and (2) may be combined, and written as:

$$\frac{dM}{dt} = -A(t)M^{\Gamma} \quad where \quad A(t) = \frac{(Q(t) + \phi\forall\lambda_s(t))C_0}{M_0^{\Gamma}} \tag{3}$$

Separating and integrating from zero to t with $M=M_o$ at $t=0$ gives a general solution for the source mass. For the special case of constant Q and $\lambda_s$, the source mass function becomes [Parker and Falta, 2008]

$$M = \left\{ \frac{(\Gamma-1)(Q+\phi\forall\lambda_s)C_0}{M_0^{\Gamma}} t + M_0^{1-\Gamma} \right\}^{\frac{1}{1-\Gamma}} \tag{4}$$

Using Equation 2, this leads to the time-dependent source discharge function:

$$C_s = \frac{C_0}{M_0^{\Gamma}} \left\{ \frac{(\Gamma-1)(Q+\phi\forall\lambda_s)C_0}{M_0^{\Gamma}} t + M_0^{1-\Gamma} \right\}^{\frac{\Gamma}{1-\Gamma}} \tag{5}$$

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):

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

and

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

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 $QC_o/M_o$, giving a source half-life of $.693M_o/(QC_o)$ (Newell and Adamson, 2005). This type of 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 (Chen 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 $\Gamma$ 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 as 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 and $\lambda_s$=0. This leads to a source concentration that declines as a linear function of time (Falta et al., 2005a; Newell and Adamson, 2005):

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

and the source completely disappears at a time of

$$t = \frac{2M_0}{QC_0} \tag{9}$$

The simplest model of source behavior is one in which $\Gamma$=0, and $\lambda_s$=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) represent source depletion by the natural process of dissolution and aqueous phase biodecay. 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, air sparging or excavation) 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 are given by:

$$M = \left\{ \frac{(\Gamma - 1)(Q + \phi\forall\lambda_s)C_2}{M_2^{\Gamma}}(t - t_2) + M_2^{1-\Gamma} \right\}^{\frac{1}{1-\Gamma}} \tag{10}$$

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

$$M_2 = (1 - \mathrm{X})M_1 \tag{12}$$

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

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 $\Gamma$. 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 3 and 4, 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 $m^3$/yr with no aqueous phase biodecay.

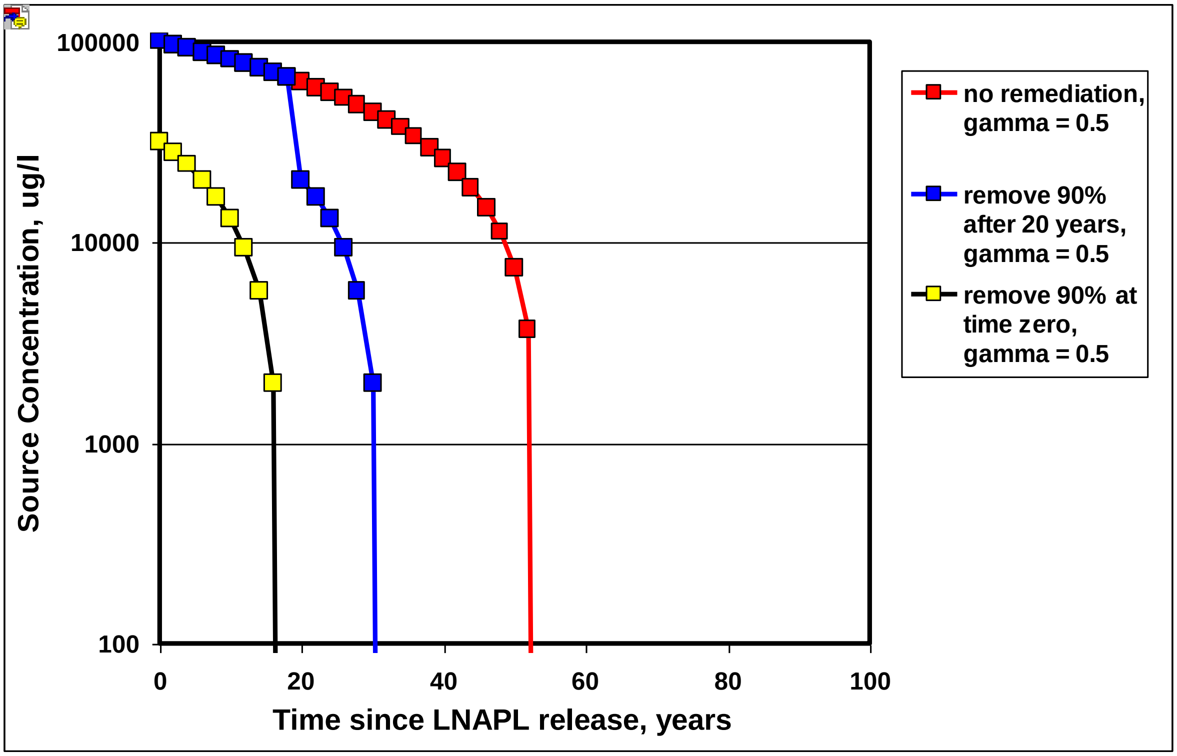


Figure 3. Source zone dissolved concentrations with and without source remediation for $\Gamma = 0.5$ (from Falta et al., 2005a)

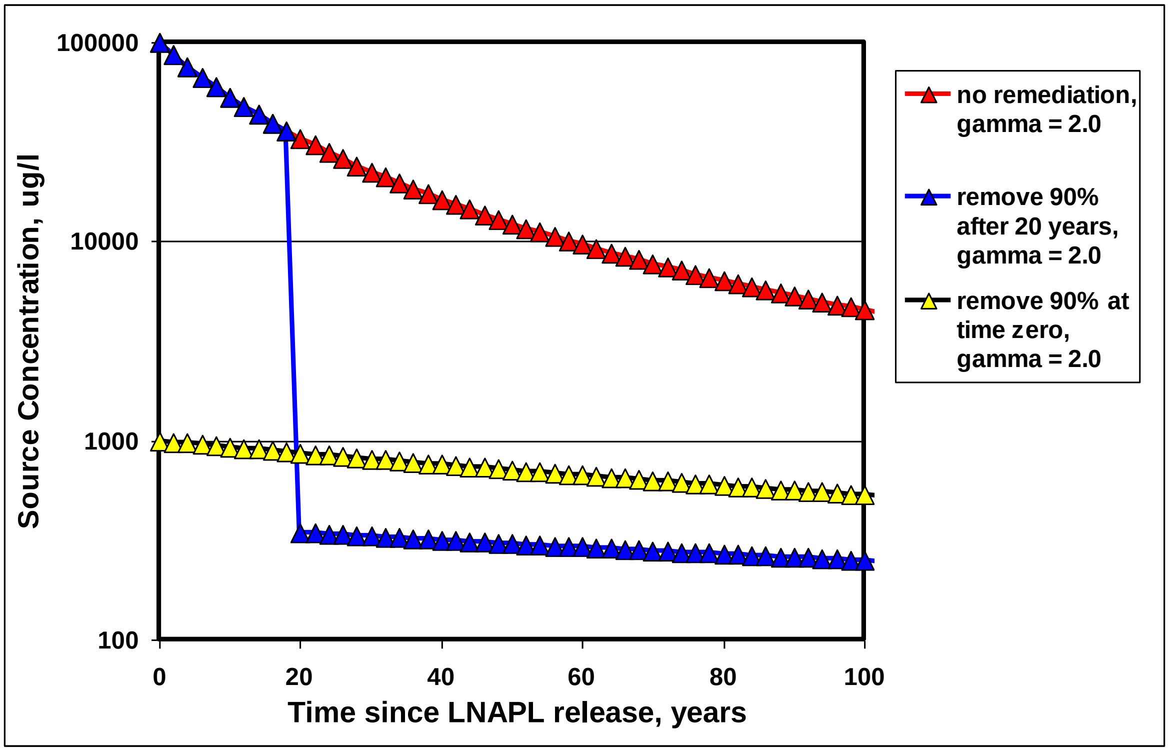


Figure 4. Source zone dissolved concentrations with and without source remediation for $\Gamma = 2.0$ (from Falta et al., 2005a)

# Coupled Plume Model with Biodegradation

The plume model for REMFuel is similar to REMChlor, except it allows zero order decay and Monod's kinetics in addition to the first order decay option in REMChlor. Falta et al. (2005b) used Equations (5) and (11) to form a mass flux boundary condition used in an advection-dispersion equation with 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, from Falta (2008) 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 natural attenuation 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 REMChlor and REMFuel models and these earlier 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:

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

where $\alpha_x$, $\alpha_y$, and $\alpha_z$ 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:

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

where *A* is the area over which the contaminant flux enters the groundwater flow system, and $\phi$ 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 (14) and (15) 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 (Falta, 2008). 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

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

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,

$$C(t)\big|_{x=0} = C_s(t) \tag{17}$$

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 5). 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.

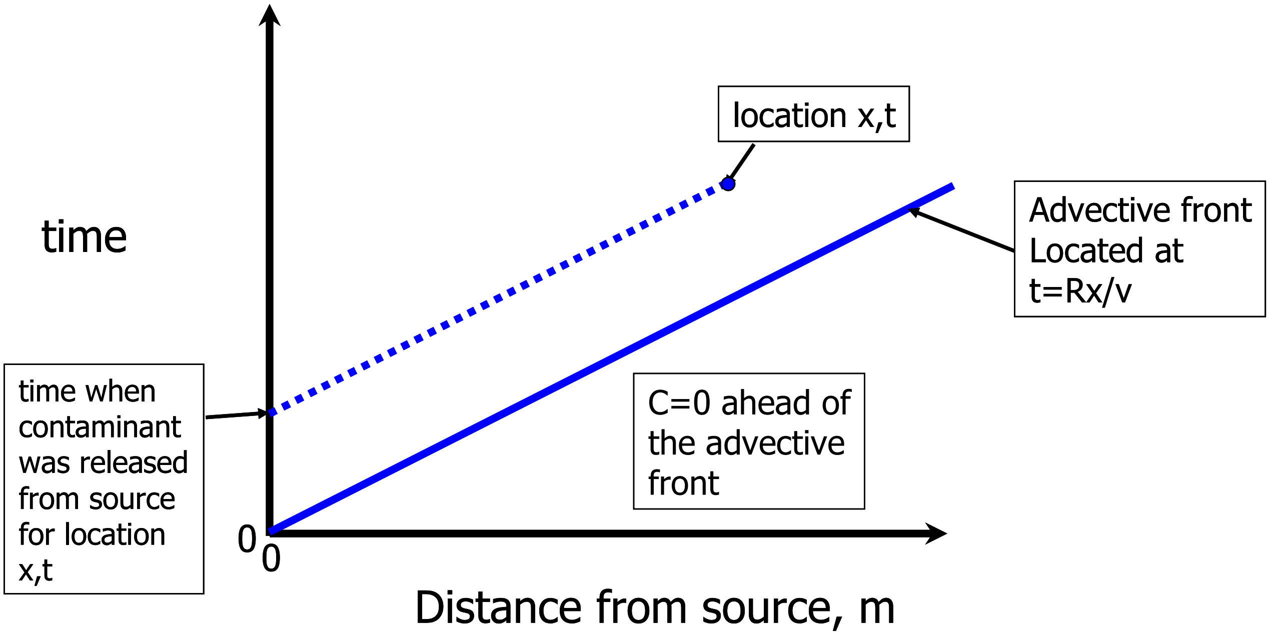


**Figure 5. Distance-time plot for advective transport with a single set of plume reaction rates**

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

$$t_{release} = t - Rx/v \tag{18}$$

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

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

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 $C(t_{release})\big|_{x=0}$ 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

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

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

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

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 the parent and daughter compounds from the decay reaction must move at the same velocity.

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 6). 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 long term conditions in the plume after manipulation of the plume ended (another period of natural attenuation).

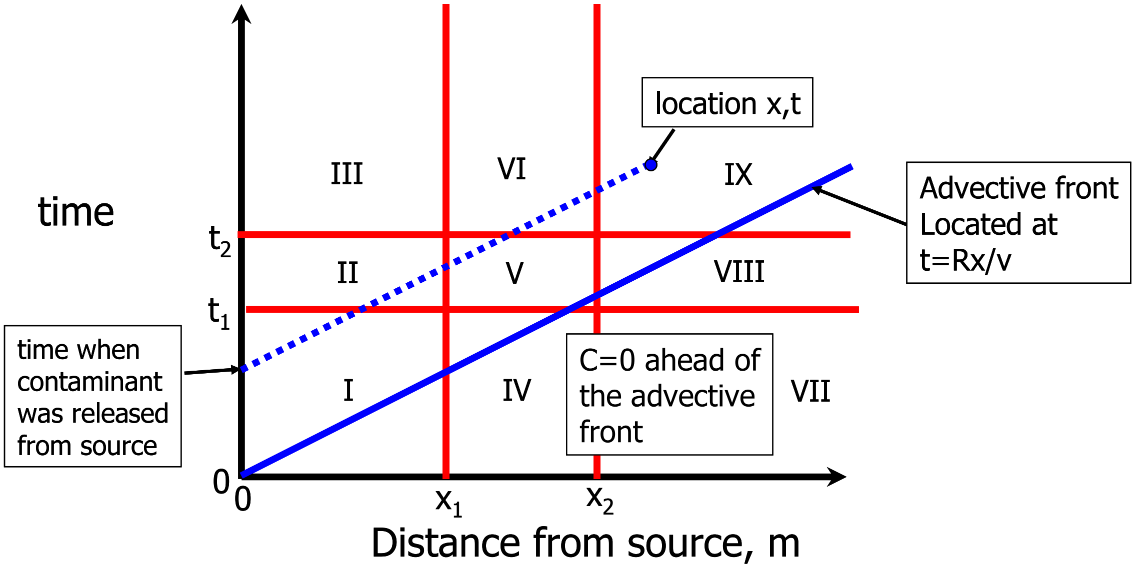


**Figure 6. Distance-time plot for advective transport with multiple sets of plume reaction rates.**

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.

An example of how these different plume reaction zones might be used is shown in Figure 7. Here it is assumed that there was a release of gasoline mixed with MTBE 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 air sparging from 400 to 700 m to treat MTBE, which moved away from the source. Downgradient of this zone, conditions might revert back to their natural state.

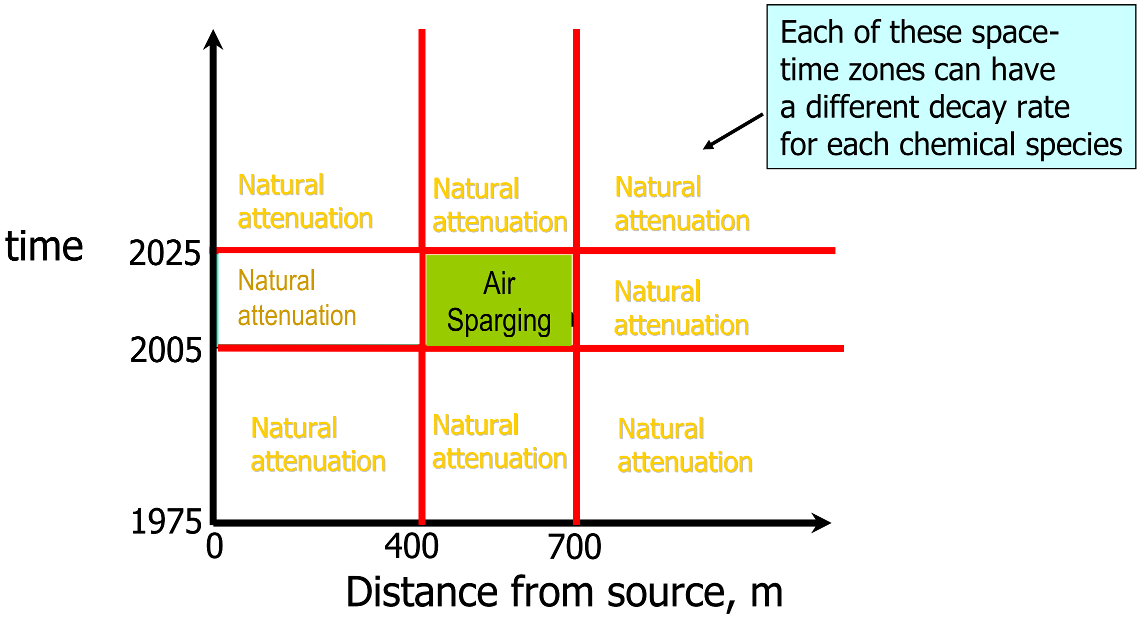


**Figure 7. Possible design of an enhanced plume remediation scheme to remediate MTBE. All other zones revert to natural background (attenuation) conditions in this example.**

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 6, 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 $C(t_{release})\big|_{x=0}$. 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:

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

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

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

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

where $y_{BA(n)}$ is the yield coefficient for the parent-daughter reaction. The yield coefficient is defined as milligrams per liter of daughter produced divided by milligrams per liter of parent consumed. Equations (23-24) 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 $C_{i(0)}=C_i(t-Rx/v)\big|_{x=0}$.

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:

$$C_{A(n)}=C_{A(n-1)}f_1(\lambda_{A(n)},t_{(n)}) \tag{25}$$

$$C_{B(n)}=C_{A(n-1)}f_2(\lambda_{A(n)},\lambda_{B(n)},y_{BA(n)},t_{(n)})+C_{B(n-1)}f_1(\lambda_{B(n)},t_{(n)}) \tag{26}$$

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

$$f_1(\lambda_1, t) = e^{-\lambda_1 t} \tag{27}$$

$$f_2(\lambda_1, \lambda_2, y_{21}, t) = y_{21}\lambda_1 \left( \frac{e^{-\lambda_1 t} - e^{-\lambda_2 t}}{\lambda_2 - \lambda_1} \right) \tag{28}$$

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 $\sigma_v$. 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)

$$P(v < v^*) = \frac{1}{\sigma_v \sqrt{2\pi}} \int_{-\infty}^{v^*} \exp\left( \frac{-(\tau - \bar{v})^2}{2\sigma_v^2} \right) d\tau = \frac{1}{2}\left( 1 + erf\left( \frac{v^* - \bar{v}}{\sigma_v \sqrt{2}} \right) \right) \tag{29}$$

This expression can be written in terms of travel distances at some time *t* by multiplying the relevant quantities in Equation (29) by *t*, and by using $x = v^* t$. 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:

$$\frac{C}{C_0} = 1 - P(vt < v^* t) = 1 - \frac{1}{2}\left[ 1 + erf\left( \frac{v^* t - \bar{v}t}{\sigma_v t \sqrt{2}} \right) \right] = \frac{1}{2} erfc\left( \frac{x - \bar{v}t}{\sigma_v t \sqrt{2}} \right) \tag{30}$$

Equation (30) 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):

$$\frac{C}{C_0} = \frac{1}{2} erfc\left( \frac{x - \bar{v}t}{2\sqrt{\alpha_x \bar{v}t}} \right) \tag{31}$$

These two expressions are equivalent if the dispersivity in Equation (31) is

$$\alpha_x = \frac{\sigma_v^2}{2\bar{v}} t = \frac{\sigma_v^2}{2\bar{v}^2} \bar{x} = a\bar{x} \tag{32}$$

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

$$\Delta v = \frac{v_{\max} - v_{\min}}{n_{tubes}} \tag{33}$$

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:

$$P(v_j < (v_j + \Delta v/2)) - P(v_j < (v_j - \Delta v/2)) \tag{34}$$

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 (34), and summed to get the solution for advection with longitudinal dispersion.

The streamtube model is compared to Equation (31) in Figure 8 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 of streamtubes (as many as 10,000) 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.

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 (34).

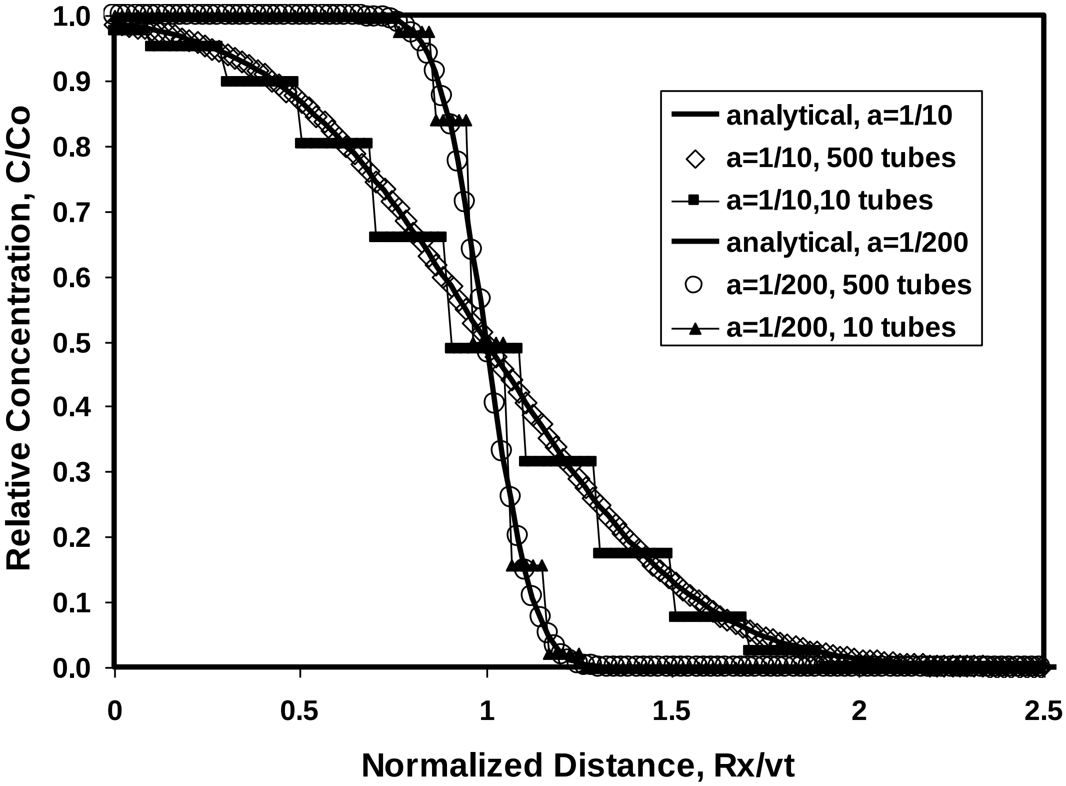


**Figure 8. Comparison of REMFuel streamtube dispersion model to error function analytical solution using a scale dependent dispersivity equal to $\alpha_x = a\bar{x}$ .**

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:

$$C(x,y,z,t) = C(x,t)\, f_y(y)\, f_z(z) \tag{35}$$

where the transverse and vertical functions are

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

$$f_z(z) = \frac{1}{2}\left( erf\left\{ \frac{z+Z}{2\sqrt{\alpha_z x}} \right\} - erf\left\{ \frac{z-Z}{2\sqrt{\alpha_z x}} \right\} \right) \tag{36}$$

This formulation assumes a 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 (36) can be altered to allow vertical dispersion in both directions (Domenico and Schwartz, 1990).

Because this dispersion method is approximate, the solutions may differ from exact solutions for transverse dispersion. Cleary and Ungs (1978) and Wexler (1992) give exact integral solutions for two-dimensional and three-dimensional dispersion problems, respectively. Comparisons of the Domenico (1987) approximation with the Cleary and Ungs (1978) solution for several examples tabulated in Javandel et al. (1984) show that the error that results from using the Domenico approximation is relatively small. Falta (2008) shows a comparison of REMChlor simulation results with the exact solution for two-dimensional advection-dispersion, and again the differences are small except for when large dispersivities are used. West et al. (2007) and Srinivasan et al (2007) provide additional analysis of possible errors resulting from the use of the Domenico approximation.

# Additional Plume Biodegradation Models

REMFuel can be used to model biodegradation in the plume through first order, zero order or Monod's kinetics. The first order parent-daughter decay option has been discussed in the previous section (see Equations 20 through 28). If the solute reaction was zero order decay in the aqueous phase with a decay rate coefficient of $\gamma$, then the equivalent batch reaction is

$$R\frac{dC}{dt} = -\gamma \quad with \quad C\big|_{t=0} = C(t_{release})\big|_{x=0} \tag{37}$$

Then at location *(x,t)* behind the front, for constant $\gamma$ the solute concentration would be

$$C(x,t) = C(t - Rx/v)\big|_{x=0} - \left(\frac{\gamma x}{v}\right) \tag{38}$$

In REMFuel, the zero order decay rate may be different in each of the nine space/time zones, and it is different for each solute in the plume. No daughter products are produced from this reaction in the model.

Monod's kinetics can also be assumed for plume biodegradation model. The rate of change in contaminant concentration according to Monod's kinetics can be given by

$$R\frac{dC}{dt} = -\mu_{\max}\frac{C}{K_c + C} \tag{39}$$

where, $\mu_{max}$ is maximum contaminant utilization rate (mg/L/d) and $K_c$ (mg/L) is the half-saturation constant or the contaminant concentration when the utilization rate is half of the maximum rate (i.e., $\mu_{max}$).

Monod's kinetics contains three regions depending on the concentration and the coefficients: first-order, zero-order, and mixed-order behavior. When $C<<K_c$, Equation 39 becomes a first-order equation with decay rate equal to $\mu_{max}/K_c$. Similarly, when $C>>K_c$, Monod's equation becomes a zero-order equation with decay rate equal to $\mu_{max}$. The intermediate region in Monod's kinetics remains as a mixed-order zone between the first and zero-order regions.

The solution of the Monod's kinetics at a location in the plume behind the advective front, with constant parameters is given by

$$\ln C(x,t) + \frac{C(x,t)}{K_c} = \ln C(t - Rx/v)\big|_{x=0} + \frac{C(t - Rx/v)\big|_{x=0}}{K_c} - \frac{\mu_{\max}\left(\frac{x}{v}\right)}{K_c} \qquad (40)$$

where $C(t\text{-}Rx/v)|_{x=0}$ is the contaminant concentration in the source at the time of release (i.e., $t_{release}$). The REMFuel model does not consider daughter production in this model, but the reaction parameters are variable functions of space and time in the plume, and are independent for each plume species. Evaluation of Equation (40) in REMFuel is done by a Newton Raphson iterative nonlinear root finding method.

# Important Limitations of REMFuel

The user should be particularly mindful of two important limitations of REMFuel.

Because REMFuel is not a distributed parameter model, it may provide misleading projections of plumes in landscapes where the hydrogeological parameters change along the extent of a potential plume of contamination. The possibility that the parameters will change increases with the size of the release and the size of the plume that would be produced from the release. The user is cautioned to compare any plume that is modeled using REMFuel to the geological context at the site to determine whether the assumptions in the model are justified over the extent of the modeled plume. As part of the peer review of REMFuel, calibration was attempted on a large spill of gasoline at a site in the intermountain west. The actual plume extended approximately 1700 feet from the point of release to the banks of a nearby river. The modeled plume was much longer, and extended across the river.

REMFuel does not account for natural attenuation of the source due to volatilization of petroleum hydrocarbons into soil gas and subsequent loss to the hydrocarbons from soil gas due to diffusion to the land surface or aerobic biodegradation in the unsaturated zone. The losses can be substantial. Ostendorf and Kampbell (1991) characterized aerobic biodegradation of aviation gasoline in the unsaturated zone above a spill and estimated that over the 20 years since the release, 39% of the original amount of gasoline that was spilled was lost by evaporation and subsequent biodegradation in the unsaturated zone.

As the elevation of the water table varies up and down, more or less of the LNAPL source area will be inundated and contribute to ground water contamination. At any point in time, that portion of the LNAPL source area that is above the water table will be subject to losses due to volatilization and biodegradation. The importance of this interaction will depend on the depth interval occupied by the LNAPL and the depth intervals occupied by excursions of the water table over time.

Loss by volatilization and subsequent biodegradation is a complex and dynamic process. At best the-state-of-science can describe the rate of overall weathering of the LNAPL source area, but cannot describe the rate of weathering of any particular constituent in the LNAPL (compare Lundegard and Johnson (2006a, 2006b)).

Because REMFuel does not consider losses to the unsaturated zone, it will overestimate the persistence of the contamination in the source area of the plume. The bias will be related to the depth of the source area used to calibrate the model (which corresponds to the depth from the water table to the bottom of the LNAPL source area) and the fraction of that depth interval that is water saturated over time.

## Input Values for Gasoline Components

Default values for 1st and zero-order plume decay rates and Monod's constants (i.e., $\mu_{max}$ and $K_c$) for different gasoline components are included in the REMFuel software. These values are obtained from literature survey on studies presenting field scale values and from using professional judgment. The following tables show the default values in REMFuel for all the decay constants and the range of values of the first-order decay rates, which is the most commonly used degradation kinetic model for gasoline compounds.

| Gasoline Compounds | Solubility (g/L) | Molecular wt. (g/mol) | Koc (L/Kg) | 1st Order Rate (per year) | Zero Order Rate (mg/L/d) | Half Saturation Constant (mg/L) | Maximum Utilization Rate (mg/L/d) |
|---|---|---|---|---|---|---|---|
| Benzene | 1.8 | 88 | 83 | 1.1 | 0.004 | 7 | 0.004 |
| Toluene | 0.53 | 92 | 300 | 20.8 | 0.54 | 10 | 0.54 |
| Ethyl Benzene | 0.15 | 106 | 1100 | 1.1 | 0.31 | 10 | 0.31 |
| *o*-Xylene | 0.13 | 106 | 830 | 19.7 | 0.62 | 6 | 0.62 |
| *m*-Xylene | 0.175 | 106 | 982 | 11 | 0.95 | 13 | 0.95 |
| *p*-Xylene | 0.198 | 106 | 870 | 13.5 | 1.58 | 16 | 1.58 |
| MTBE | 48 | 88* | 11 | 1.2 | 0.2 | 30 | 0.2 |
| TBA | 780 | 74 | 15 | 7 | 2 | 50 | 2 |
| TAME | 20 | 102 | 102 | 1.2 | 0.2 | 30 | 0.2 |
| DIPE | 9 | 102 | 102 | 0 | 0 | Not Applicable | Not Applicable |
| ETBE | 26 | 102 | 102 | 0 | 0 | Not Applicable | Not Applicable |
| Naphthalene | 0.03 | 128 | 1300 | 1 | Not Applicable | Not Applicable | Not Applicable |
| EDB | 4.3 | 188 | 44 | 0.63 | Not Applicable | Not Applicable | Not Applicable |
| 1,2-DCA | 8.7 | 98.9 | 14 | 0.71 | Not Applicable | Not Applicable | Not Applicable |

* REMFuel has 78 for MTBE. The user can change this in the program.

| Gasoline Compounds | 1st Order Rate (per year) | Range | References |
|---|---|---|---|
| Benzene | 1.1 | 0.1 - 28 | Suarez and Rifai (1999); Reinhard et al. (2005) |
| Toluene | 20.8 | 0.1 – 68 | Suarez and Rifai (1999); Reinhard et al. (2005) |
| Ethyl Benzene | 1.1 | 0.1 - 20 | Suarez and Rifai (1999); Reinhard et al. (2005) |
| *o*-Xylene | 19.7 | 0.1 - 78 | Suarez and Rifai (1999); Reinhard et al. (2005) |
| *m*-Xylene | 11 | 0.1 - 38 | Suarez and Rifai (1999); Reinhard et al. (2005) |
| *p*-Xylene | 13.5 | 0.1 - 29 | Suarez and Rifai (1999); Reinhard et al. (2005) |
| MTBE | 1.2 | 0 - 2 | Wilson et al. (2005); Mormile et al. (1994) |
| TBA | 7 | 1 - 9 | Wilson and Adair (2007) |
| TAME | 1.2 | 0 - 2 | Mormile et al. (1994); Somsamak et al. (2005); Professional Judgment [ζ] |
| DIPE | 0 | - | Mormile et al. (1994) |
| ETBE | 0 | - | Mormile et al. (1994) |
| Naphthalene | 1 | 0.1 – 19 | Lewandowski and Mortimer (2003); Greve (2007) |
| EDB | 0.63 | 0.22 – 1.3 | Wilson et al. (2008) |
| 1,2-DCA | 0.71 | 0.22 – 0.9 | Wilson et al. (2008) |

[ζ] Assumed same as MTBE according to **John T. Wilson**, Senior Microbiologist, GWERD, NRMRL, USEPA, Ada, Oklahoma.

Gasoline composition data are collected from Weaver et al. (2005) and Potter and Simmons (1998). A nationwide gasoline study was conducted by Weaver et al. (2005). Samples were collected from active gas stations in U.S. states that used conventional and reformulated gasoline. Until 2006 reformulated gasoline was required to contain oxygen at 2% by weight and benzene was required to be less than 1% by volume. Conventional gasoline had limits on benzene content that were set by producer baselines. These gasoline products sometimes contain oxygenated additives, because they serve to boost the octane rating of the fuel (Weaver et al., 2010). The following table shows the mass fraction of some key gasoline components for different types of gasoline and oil products.

| Compound mass fraction | Benzene | Toluene | Ethyl Benzene | *o*-Xylene | *m*-Xylene | *p*-Xylene | MTBE | TBA | TAME | DIPE | ETBE | Napthalene | EDB | 1,2-DCA | NAPL density (kg/L) | NAPL mol. wt. (g/mol) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Gasoline (unleaded with high MTBE) | 0.006 | 0.059 | 0.01 | 0.051 | 0.051 | 0.051 | 0.12 | NAA[ζ] | 0 | 0 | NAA | 0.0003 | NAA | NAA | 0.72 | 105 |
| Gasoline (unleaded with low MTBE) | 0.0075 | 0.08 | 0.013 | 0.07 | 0.07 | 0.07 | 0.013 | NAA | 0 | 0 | NAA | 0.0003 | NAA | NAA | 0.72 | 105 |
| Reformulated Regular Grade Gasoline | 0.0066 | 0.0506 | 0.0162 | 0.0147 | 0.0267 | 0.0109 | 0.097 | NAA | 0.003 | 0 | NAA | 0.0053 | NAA | NAA | 0.72 | 105 |
| Reformulated Premium Grade Gasoline | 0.0043 | 0.057 | 0.0118 | 0.0167 | 0.0274 | 0.0121 | 0.01 | NAA | 0.004 | 0 | NAA | 0.0038 | NAA | NAA | 0.72 | 105 |
| Reformulated Regular Grade Gasoline (MTBE ban States) | 0.0076 | 0.0497 | 0.0103 | 0.0147 | 0.0273 | 0.011 | 0.002 | NAA | 0 | 0 | NAA | 0.0028 | NAA | NAA | 0.72 | 105 |
| Reformulated Premium Grade Gasoline (MTBE ban States) | 0.0073 | 0.0102 | 0.0179 | 0.0247 | 0.0432 | 0.019 | 0.002 | NAA | 0.01 | 0 | NAA | 0.0028 | NAA | NAA | 0.72 | 105 |
| Conventional Regular Grade Gasoline (Elevation <1000 ft MSL) | 0.0145 | 0.1037 | 0.0224 | 0.0237 | 0.0433 | 0.019 | 0.005 | NAA | 4E-04 | 0 | NAA | 0.004 | NAA | NAA | 0.72 | 105 |
| Conventional Premium Grade Gasoline (Elevation <1000 ft MSL) | 0.0082 | 0.1423 | 0.0153 | 0.0184 | 0.0325 | 0.015 | 0.033 | NAA | 0.005 | 0 | NAA | 0.0043 | NAA | NAA | 0.72 | 105 |

[ζ] NAA means No Analysis Available. REMFuel inputs zero as default value in place of NAA. The users have the option to change the default values.

| Compound mass fraction | Benzene | Toluene | Ethyl Benzene | *o*-Xylene | *m*-Xylene | *p*-Xylene | MTBE | TBA | TAME | DIPE | ETBE | Napthalene | EDB | 1,2-DCA | NAPL density (kg/L) | NAPL mol. wt. (g/mol) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Conventional Regular Grade Gasoline (Elevation >3000 ft MSL) | 0.0166 | 0.0676 | 0.0144 | 0.0203 | 0.0385 | 0.0168 | 0.001 | NAA[ζ] | 0 | 0 | NAA | 0.0038 | NAA | NAA | 0.72 | 105 |
| Conventional Premium Grade Gasoline (Elevation >3000 ft MSL) | 0.0159 | 0.0644 | 0.0118 | 0.017 | 0.0321 | 0.014 | 5E-04 | NAA | 0 | 0 | NAA | 0.0028 | NAA | NAA | 0.72 | 105 |
| Diesel | 0.00026 | 0.0003 | 0.00017 | 0.00302 | 0.00302 | 0.00302 | NAA | NAA | NAA | NAA | NAA | 0.0006 | NAA | NAA | 0.84 | 230 |
| Diesel #2 | 0.00029 | 0.0018 | 0.00068 | 0.00043 | 0.0011 | 0.0011 | NAA | NAA | NAA | NAA | NAA | 0.0026 | NAA | NAA | 0.84 | 230 |
| Jet fuel JP-4 | 0.0047 | 0.016 | 0.0066 | 0.01 | 0.0096 | 0.0035 | NAA | NAA | NAA | NAA | NAA | 0.0025 | NAA | NAA | 0.85 | 165 |
| Jet fuel JP-5 | 0 | 0 | 0 | 0.0009 | 0.0013 | 0 | NAA | NAA | NAA | NAA | NAA | 0.0057 | NAA | NAA | 0.85 | 165 |
| Jet fuel JP-7 | 0 | 0 | 0 | 0 | 0 | 0 | NAA | NAA | NAA | NAA | NAA | 0.0072 | NAA | NAA | 0.85 | 165 |
| Jet fuel JP-8 | 0 | 0 | 0 | 0.0006 | 0.0006 | 0 | NAA | NAA | NAA | NAA | NAA | 0.011 | NAA | NAA | 0.85 | 165 |
| Kerosene | 0 | 0 | 0 | 0 | 0 | 0 | NAA | NAA | NAA | NAA | NAA | 0.0031 | NAA | NAA | 0.85 | 170 |
| Fuel oil #2 | 0 | 0.0006 | 0.00034 | 0.0008 | 0.0008 | 0.0008 | NAA | NAA | NAA | NAA | NAA | 0.0022 | NAA | NAA | 0.94 | 250 |
| Fuel oil #6 | 0 | 0 | 0 | 0 | 0 | 0 | NAA | NAA | NAA | NAA | NAA | 0.000042 | NAA | NAA | 0.94 | 250 |
| Lubricating and Motor Oil | 0.00096 | 0.0022 | 0.0011 | 0.0011 | 0.0011 | 0 | NAA | NAA | NAA | NAA | NAA | 0.00059 | NAA | NAA | 0.94 | 250 |
| Crude oil | 0.0016 | 0.0067 | 0.0017 | 0.0026 | 0.0066 | 0.0026 | NAA | NAA | NAA | NAA | NAA | 0.00069 | NAA | NAA | 0.88 | 250 |
| Gasoline Fuel Oil | 0.019 | 0.081 | 0.017 | 0.025 | 0.046 | 0.019 | 0.003 | NAA | NAA | NAA | NAA | 0.0025 | NAA | NAA | 0.72 | 105 |

[ζ] NAA means No Analysis Available. REMFuel inputs zero as default value in place of NAA. The users have the option to change the default values.

# Graphical User Interface

## Projects Tab

When REMFuel is started (by double clicking on the application icon), the default project, “REMFuel”, 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 “REMFuel 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).

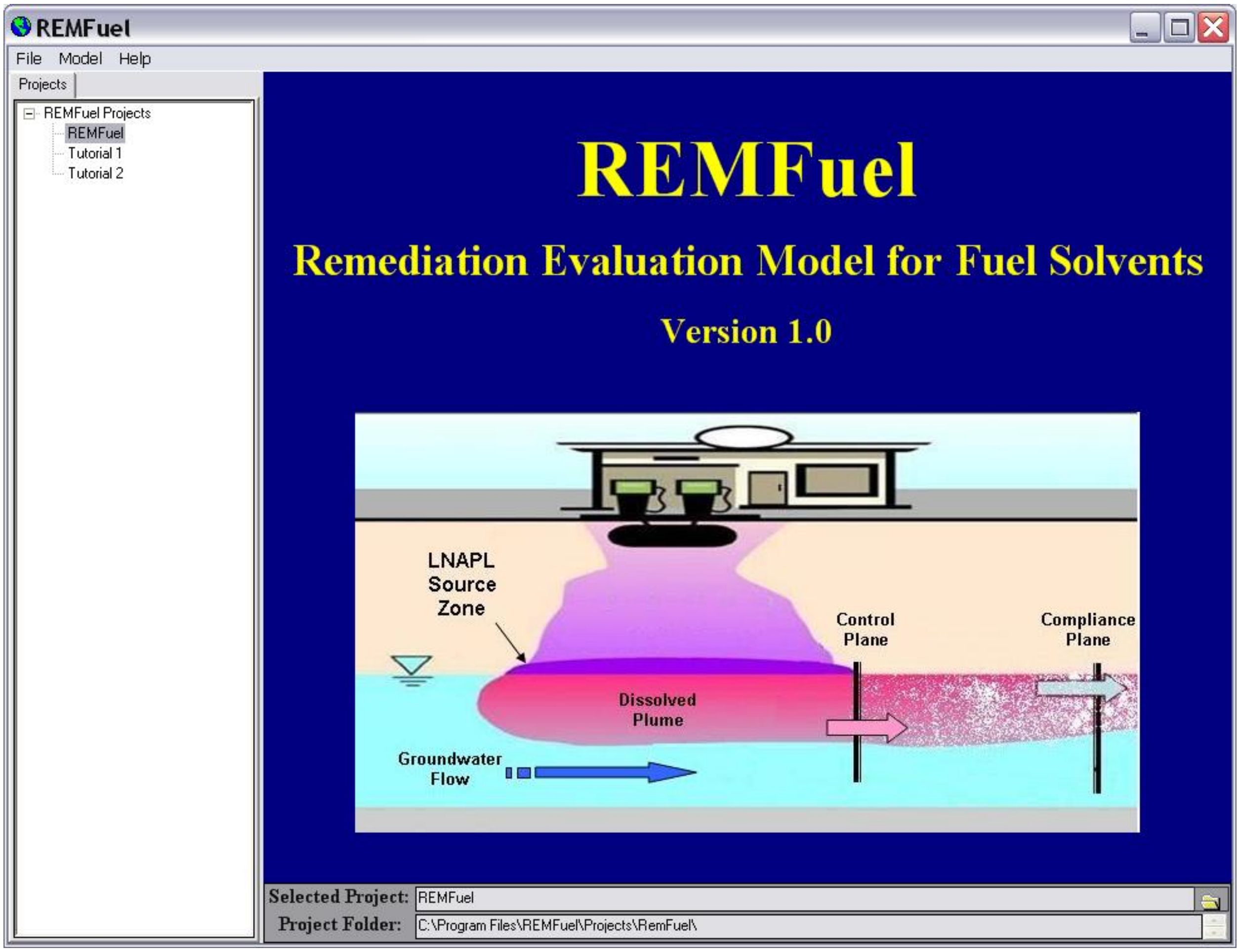
### View Graphical Output

Concentration or mass discharge versus distance in the x-direction for any value of time, t can be viewed graphically by clicking on “Output vs Distance” under “View Graphical Output”. The users can view the output along any later section and any vertical layer by selecting the Y and Z tabs in the output window. Model output can also be viewed in a spreadsheet format that shows the concentration or mass discharge output at any instant and space i.e., (x,y,z,t) by clicking the ‘Output Data’ tab.

# Basic Operation

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

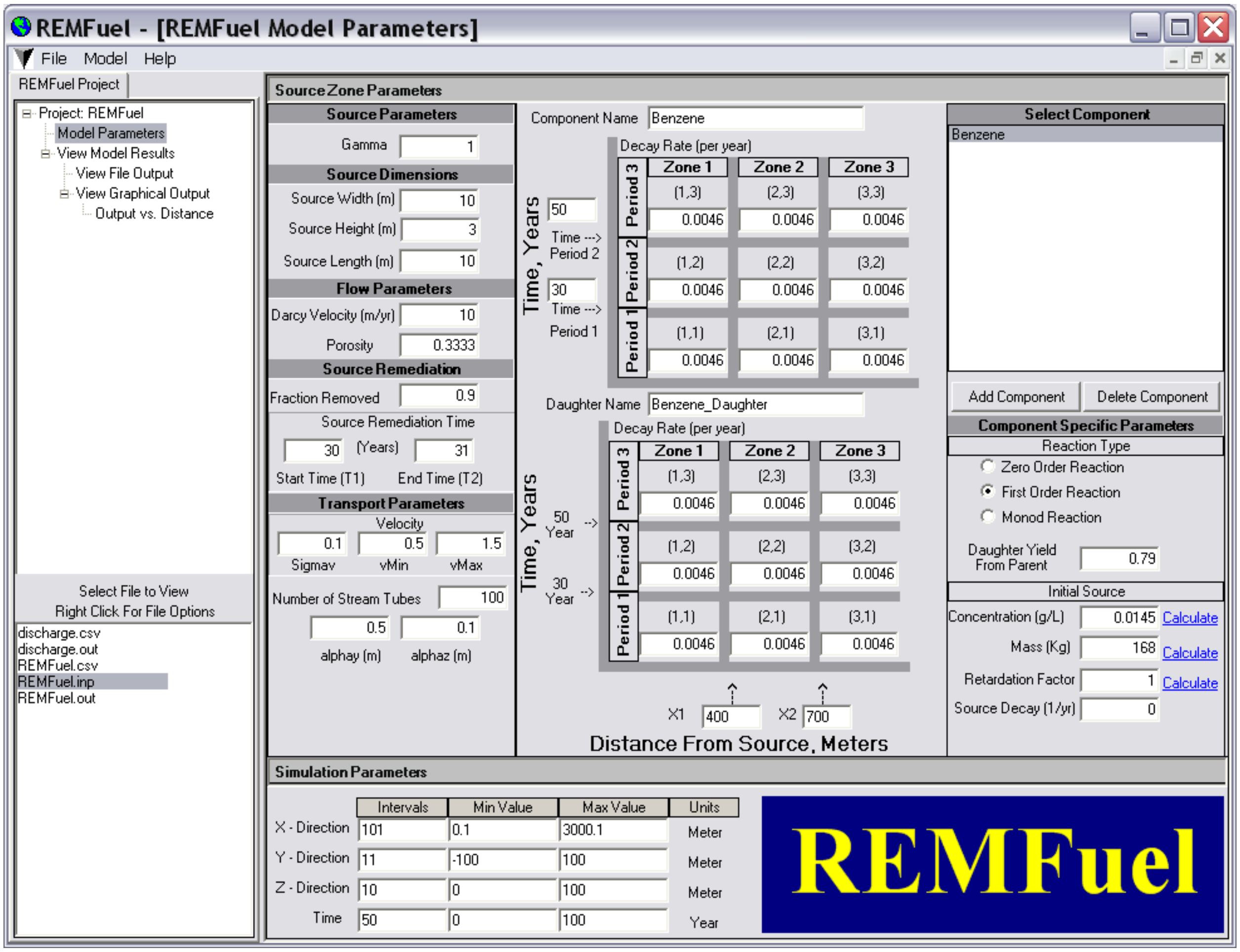
1. Double-click the REMFuel icon on your desktop to start the application. You will see the following screen:



Selected Project: REMFuel

Project Folder: C:\Program Files\REMFuel\Projects\RemFuel\

2. Double-click on “REMFuel” under REMFuel Projects and you will see the Model Parameters screen:



**Source Zone Parameters**

**Source Parameters**

Gamma 1

**Source Dimensions**

Source Width (m) 10

Source Height (m) 3

Source Length (m) 10

**Flow Parameters**

Darcy Velocity (m/yr) 10

Porosity 0.3333

**Source Remediation**

Fraction Removed 0.9

Source Remediation Time: Start Time (T1) 30 (Years) End Time (T2) 31

**Transport Parameters**

Velocity: Sigmav 0.1, vMin 0.5, vMax 1.5

Number of Stream Tubes 100

alphay (m) 0.5, alphaz (m) 0.1

Component Name Benzene

Decay Rate (per year)

Time, Years: 50 Time ---> Period 2; 30 Time ---> Period 1

| | Zone 1 | Zone 2 | Zone 3 |
|---|---|---|---|
| Period 3 | (1,3)<br>0.0046 | (2,3)<br>0.0046 | (3,3)<br>0.0046 |
| Period 2 | (1,2)<br>0.0046 | (2,2)<br>0.0046 | (3,2)<br>0.0046 |
| Period 1 | (1,1)<br>0.0046 | (2,1)<br>0.0046 | (3,1)<br>0.0046 |

Daughter Name Benzene_Daughter

Decay Rate (per year)

Time, Years: 50 Year -->; 30 Year -->

| | Zone 1 | Zone 2 | Zone 3 |
|---|---|---|---|
| Period 3 | (1,3)<br>0.0046 | (2,3)<br>0.0046 | (3,3)<br>0.0046 |
| Period 2 | (1,2)<br>0.0046 | (2,2)<br>0.0046 | (3,2)<br>0.0046 |
| Period 1 | (1,1)<br>0.0046 | (2,1)<br>0.0046 | (3,1)<br>0.0046 |

X1 400 X2 700

Distance From Source, Meters

**Select Component**

Benzene

**Component Specific Parameters**

Reaction Type

○ Zero Order Reaction

● First Order Reaction

○ Monod Reaction

Daughter Yield From Parent 0.79

Initial Source

Concentration (g/L) 0.0145

Mass (Kg) 168

Retardation Factor 1

Source Decay (1/yr) 0

**Simulation Parameters**

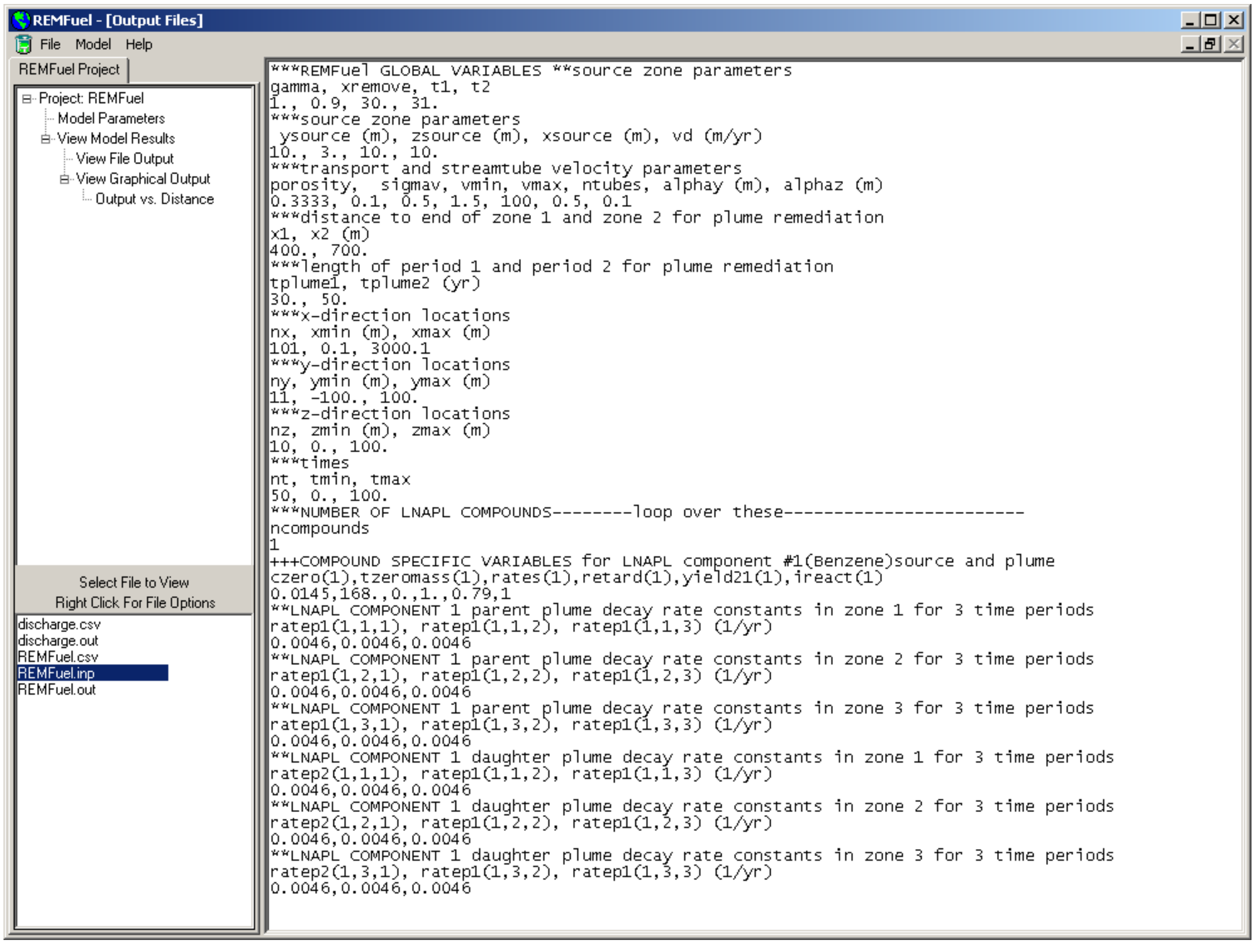
| | Intervals | Min Value | Max Value | Units |
|---|---|---|---|---|
| X - Direction | 101 | 0.1 | 3000.1 | Meter |
| Y - Direction | 11 | -100 | 100 | Meter |
| Z - Direction | 10 | 0 | 100 | Meter |
| Time | 50 | 0 | 100 | Year |

The parameters are set to run the REMFuel sample problem. As you move the mouse over the input boxes, a simple explanation of the input is provided in pop-up boxes.

From the Model pull-down menu, click “Run”. 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”.

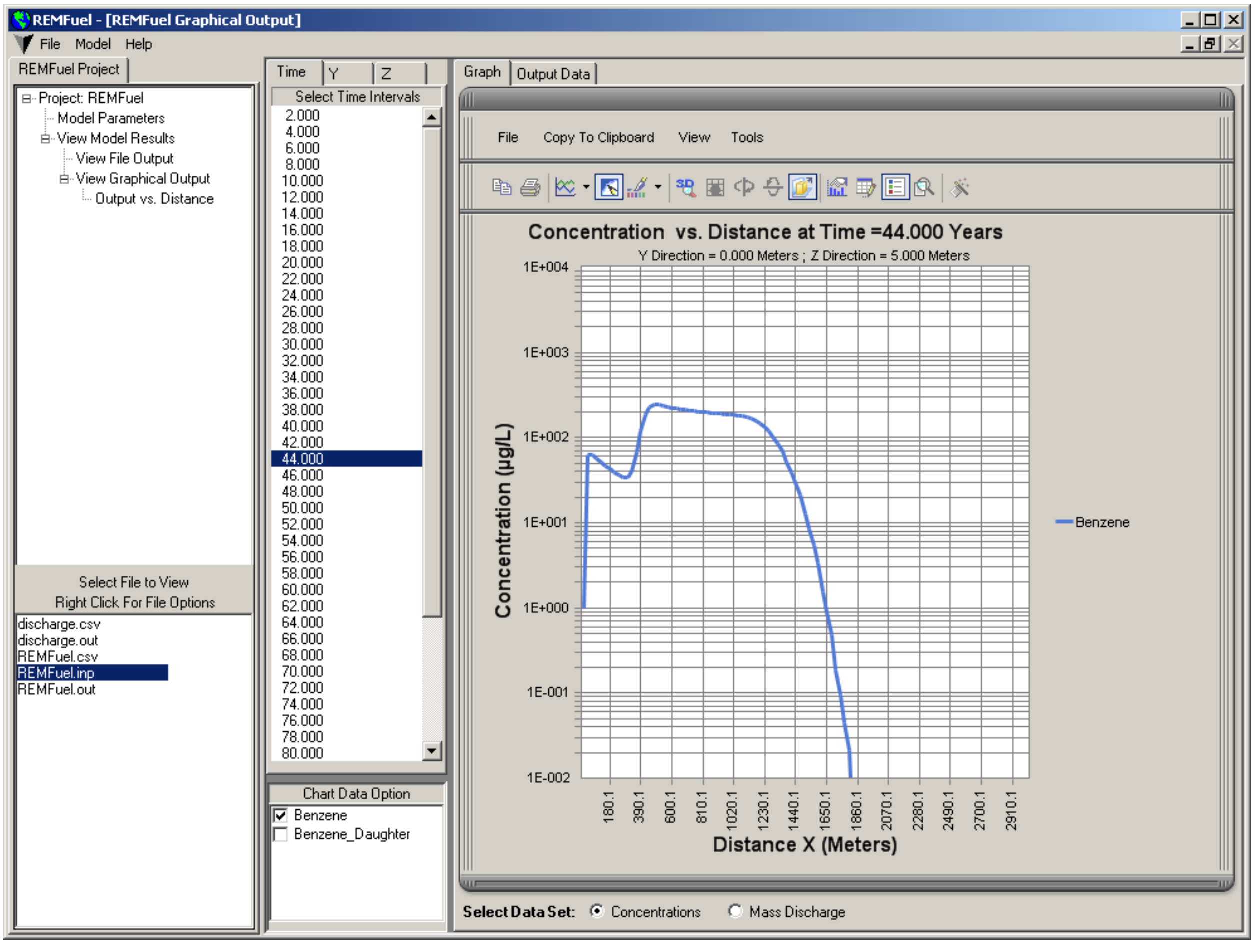
The “Help” menu has the links to view the user’s manual and to open the indexed help window, which was created from the user’s manual.

This is what you will see if you choose “REMFuel.inp” to view:  This is the formatted text file that is used as the input to the FORTRAN code that computes the analytical solution.



```
***REMFuel GLOBAL VARIABLES **source zone parameters
gamma, xremove, t1, t2
1., 0.9, 30., 31.
***source zone parameters
 ysource (m), zsource (m), xsource (m), vd (m/yr)
10., 3., 10., 10.
***transport and streamtube velocity parameters
porosity,  sigmav, vmin, vmax, ntubes, alphay (m), alphaz (m)
0.3333, 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.
***x-direction locations
nx, xmin (m), xmax (m)
101, 0.1, 3000.1
***y-direction locations
ny, ymin (m), ymax (m)
11, -100., 100.
***z-direction locations
nz, zmin (m), zmax (m)
10, 0., 100.
***times
nt, tmin, tmax
50, 0., 100.
***NUMBER OF LNAPL COMPOUNDS--------loop over these------------------------
ncompounds
1
+++COMPOUND SPECIFIC VARIABLES for LNAPL component #1(Benzene)source and plume
czero(1),tzeromass(1),rates(1),retard(1),yield21(1),ireact(1)
0.0145,168.,0.,1.,0.79,1
**LNAPL COMPONENT 1 parent plume decay rate constants in zone 1 for 3 time periods
ratep1(1,1,1), ratep1(1,1,2), ratep1(1,1,3) (1/yr)
0.0046,0.0046,0.0046
**LNAPL COMPONENT 1 parent plume decay rate constants in zone 2 for 3 time periods
ratep1(1,2,1), ratep1(1,2,2), ratep1(1,2,3) (1/yr)
0.0046,0.0046,0.0046
**LNAPL COMPONENT 1 parent plume decay rate constants in zone 3 for 3 time periods
ratep1(1,3,1), ratep1(1,3,2), ratep1(1,3,3) (1/yr)
0.0046,0.0046,0.0046
**LNAPL COMPONENT 1 daughter plume decay rate constants in zone 1 for 3 time periods
ratep2(1,1,1), ratep1(1,1,2), ratep1(1,1,3) (1/yr)
0.0046,0.0046,0.0046
**LNAPL COMPONENT 1 daughter plume decay rate constants in zone 2 for 3 time periods
ratep2(1,2,1), ratep1(1,2,2), ratep1(1,2,3) (1/yr)
0.0046,0.0046,0.0046
**LNAPL COMPONENT 1 daughter plume decay rate constants in zone 3 for 3 time periods
ratep2(1,3,1), ratep1(1,3,2), ratep1(1,3,3) (1/yr)
0.0046,0.0046,0.0046
```

Clicking on “Output vs Distance” under “View Graphical Output”, and selecting Time as 44 will bring up the following screen:



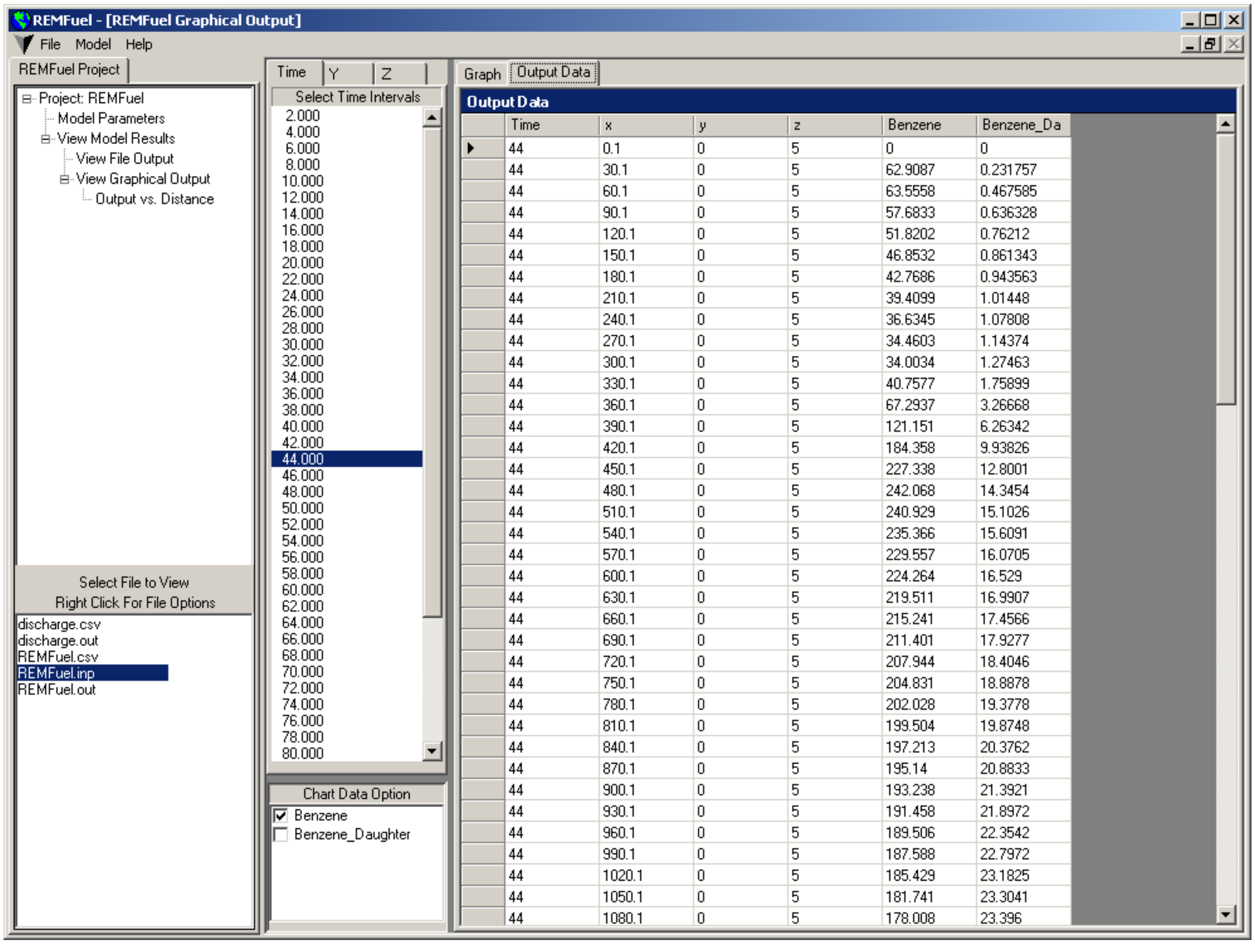
Time: 44.000

☑ Benzene
☐ Benzene_Daughter

**Select Data Set:** ● Concentrations ○ Mass Discharge

Within this window, the user has access to a fully functioning suite of user-friendly and powerful graphics tools for viewing, manipulating, and saving output images.

Clicking on the “Output Data” tab above the graph will display the output in a spreadsheet format.



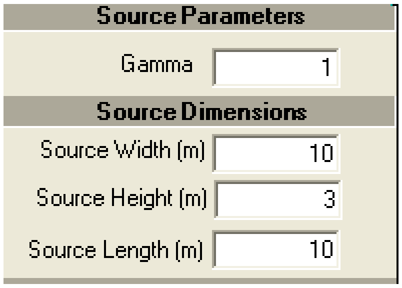
Output Data

| Time | x | y | z | Benzene | Benzene_Da |
|---|---|---|---|---|---|
| 44 | 0.1 | 0 | 5 | 0 | 0 |
| 44 | 30.1 | 0 | 5 | 62.9087 | 0.231757 |
| 44 | 60.1 | 0 | 5 | 63.5558 | 0.467585 |
| 44 | 90.1 | 0 | 5 | 57.6833 | 0.636328 |
| 44 | 120.1 | 0 | 5 | 51.8202 | 0.76212 |
| 44 | 150.1 | 0 | 5 | 46.8532 | 0.861343 |
| 44 | 180.1 | 0 | 5 | 42.7686 | 0.943563 |
| 44 | 210.1 | 0 | 5 | 39.4099 | 1.01448 |
| 44 | 240.1 | 0 | 5 | 36.6345 | 1.07808 |
| 44 | 270.1 | 0 | 5 | 34.4603 | 1.14374 |
| 44 | 300.1 | 0 | 5 | 34.0034 | 1.27463 |
| 44 | 330.1 | 0 | 5 | 40.7577 | 1.75899 |
| 44 | 360.1 | 0 | 5 | 67.2937 | 3.26668 |
| 44 | 390.1 | 0 | 5 | 121.151 | 6.26342 |
| 44 | 420.1 | 0 | 5 | 184.358 | 9.93826 |
| 44 | 450.1 | 0 | 5 | 227.338 | 12.8001 |
| 44 | 480.1 | 0 | 5 | 242.068 | 14.3454 |
| 44 | 510.1 | 0 | 5 | 240.929 | 15.1026 |
| 44 | 540.1 | 0 | 5 | 235.366 | 15.6091 |
| 44 | 570.1 | 0 | 5 | 229.557 | 16.0705 |
| 44 | 600.1 | 0 | 5 | 224.264 | 16.529 |
| 44 | 630.1 | 0 | 5 | 219.511 | 16.9907 |
| 44 | 660.1 | 0 | 5 | 215.241 | 17.4566 |
| 44 | 690.1 | 0 | 5 | 211.401 | 17.9277 |
| 44 | 720.1 | 0 | 5 | 207.944 | 18.4046 |
| 44 | 750.1 | 0 | 5 | 204.831 | 18.8878 |
| 44 | 780.1 | 0 | 5 | 202.028 | 19.3778 |
| 44 | 810.1 | 0 | 5 | 199.504 | 19.8748 |
| 44 | 840.1 | 0 | 5 | 197.213 | 20.3762 |
| 44 | 870.1 | 0 | 5 | 195.14 | 20.8833 |
| 44 | 900.1 | 0 | 5 | 193.238 | 21.3921 |
| 44 | 930.1 | 0 | 5 | 191.458 | 21.8972 |
| 44 | 960.1 | 0 | 5 | 189.506 | 22.3542 |
| 44 | 990.1 | 0 | 5 | 187.588 | 22.7972 |
| 44 | 1020.1 | 0 | 5 | 185.429 | 23.1825 |
| 44 | 1050.1 | 0 | 5 | 181.741 | 23.3041 |
| 44 | 1080.1 | 0 | 5 | 178.008 | 23.396 |

# Model Input Variables

## LNAPL Source Parameters in REMFuel

### Basic Source Parameters



Gamma: 1

Source Width (m): 10

Source Height (m): 3

Source Length (m): 10

*Gamma* = power function exponent $\Gamma$ in the source concentration versus mass function. See the '**LNAPL source model in REMFuel**' section for detail on this parameter (also see Figures 2-4). For a constant concentration source, *Gamma* = 0 and for an exponentially decaying source *Gamma* = 1.

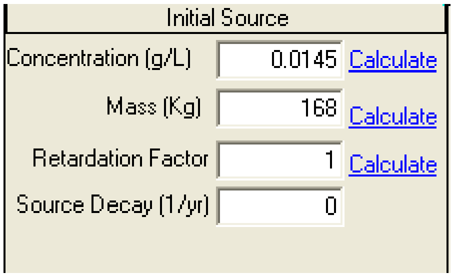
*Source Width* = source zone width perpendicular to flow, Y, *m*

*Source Height* = vertical thickness of source zone, *Z*, *m*

> This is the vertical thickness from the elevation of the mean annual water table to elevation of the bottom of the source zone contaminated with LNAPL.

*Source Length* = source zone length in the direction of flow, *X*, *m*

## Source Parameters Related to the Chemical of Concern



Initial Source

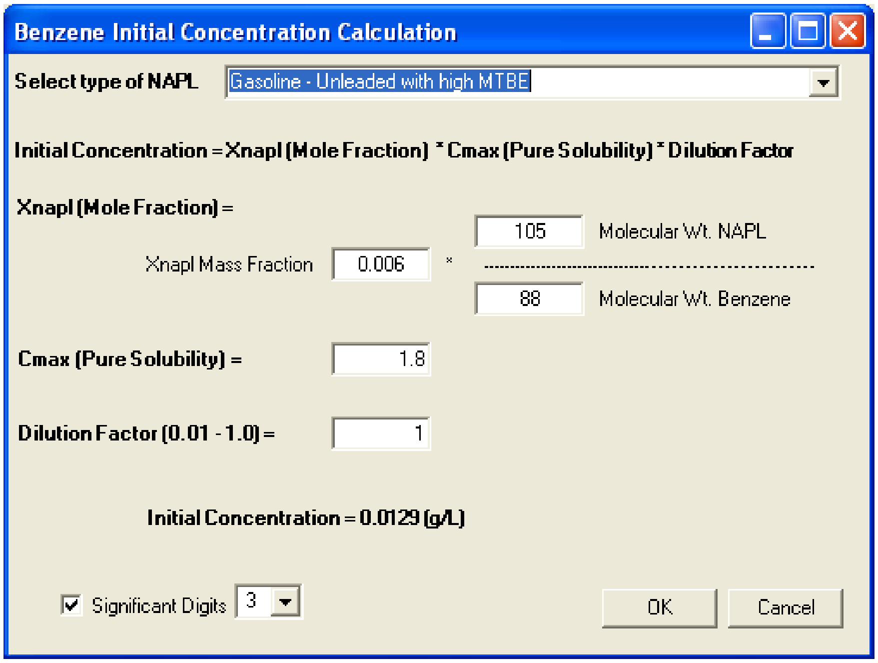
Concentration (g/L): 0.0145

Mass (Kg): 168

Retardation Factor: 1

Source Decay (1/yr): 0

*Concentration* = initial source zone concentration; $C_0$; flow averaged concentration of LNAPL chemical leaving the source zone, g/L. Initial source mass can be estimated by clicking the ‘Calculate’ link next to the concentration input box. The following screen will pop-up.



Benzene Initial Concentration Calculation

Select type of NAPL: Gasoline - Unleaded with high MTBE

Initial Concentration = Xnapl (Mole Fraction) * Cmax (Pure Solubility) * Dilution Factor

Xnapl (Mole Fraction) =

Xnapl Mass Fraction: 0.006 * (Molecular Wt. NAPL: 105) / (Molecular Wt. Benzene: 88)

Cmax (Pure Solubility) = 1.8

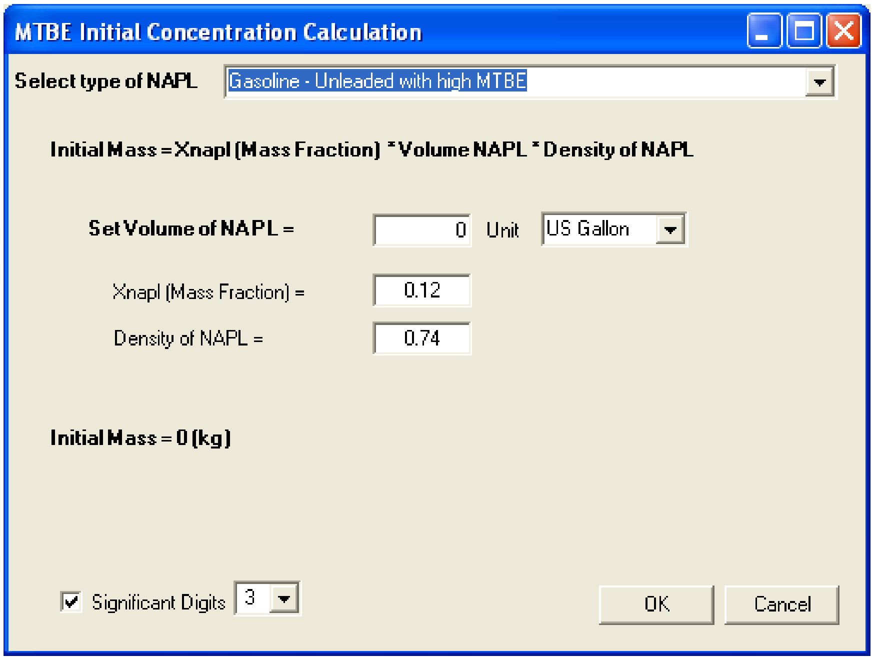
Dilution Factor (0.01 - 1.0) = 1

Initial Concentration = 0.0129 (g/L)

☑ Significant Digits: 3

The user needs to select the type of NAPL from the drop-down menu to get an estimate of initial concentration for the chemical of concern. Also, the user has the option to change the initial estimate during the calibration process.

*Mass* = initial source zone contaminant mass, $M_0$, kg. This value can be estimated by clicking the ‘Calculate’ link next to the mass input box. The following screen will pop-up.



Select type of NAPL: Gasoline - Unleaded with high MTBE

Initial Mass = Xnapl (Mass Fraction) * Volume NAPL * Density of NAPL

Set Volume of NAPL = 0 Unit US Gallon

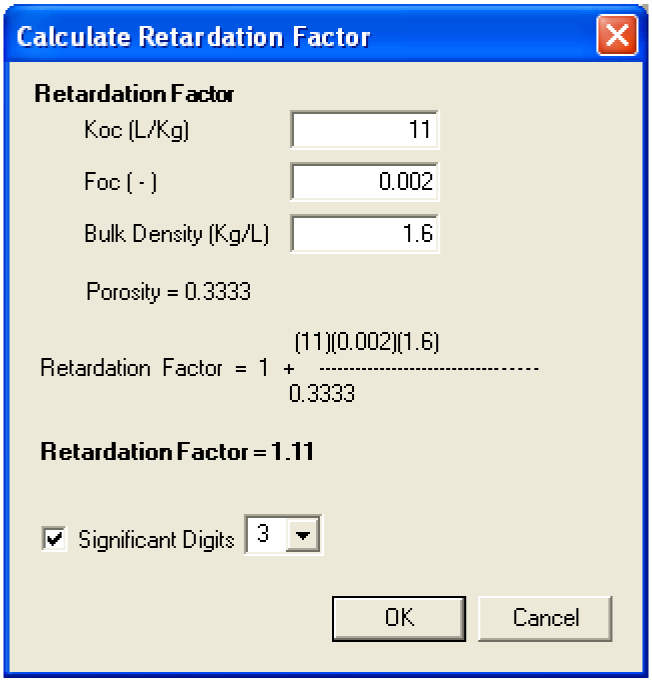
Xnapl (Mass Fraction) = 0.12

Density of NAPL = 0.74

Initial Mass = 0 (kg)

☑ Significant Digits 3

*Retardation Factor* = Retardation factor for each dissolved species, *R*. Different values of retardation can be assigned to different chemicals of concern. However, it is assumed to be the same for parent-daughter components. The retardation factor for each chemical of concern can be estimated by clicking the ‘Calculate’ link next to the mass input box. The following screen will pop-up.



Retardation Factor

Koc (L/Kg) 11

Foc ( - ) 0.002

Bulk Density (Kg/L) 1.6

Porosity = 0.3333

$$\text{Retardation Factor} = 1 + \frac{(11)(0.002)(1.6)}{0.3333}$$

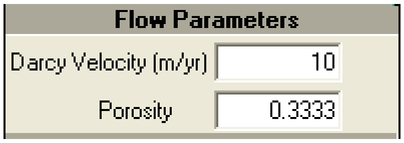
Retardation Factor = 1.11

☑ Significant Digits 3

Organic carbon partition coefficient ($K_{OC}$), soil fraction of organic carbon ($F_{OC}$), bulk density of soil, and porosity input are required to get the initial estimate of *R*. The user has the option to change the initial estimate during the calibration process.

*Source Decay* = First order aqueous phase biodecay of the component in the source zone, $\lambda_s$, 1/yr

# Flow Parameters



Flow Parameters

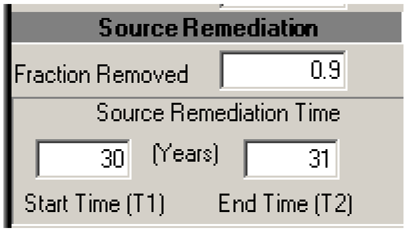
Darcy Velocity (m/yr) 10

Porosity 0.3333

*Darcy Velocity* = Darcy flux (velocity) in the flow system, $V$, m/yr. The chemical velocity without retardation due to sorption, (which is also the pore velocity, $v$) is equal to the Darcy velocity divided by the porosity ( $\phi$ ). The total flow rate through the source zone, $Q=VYZ$.

*Porosity* = effective porosity, $\phi$

# Source Remediation



Source Remediation

Fraction Removed 0.9

Source Remediation Time

Start Time (T1) 30 (Years)

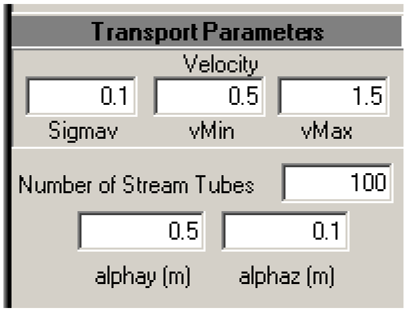
End Time (T2) 31

*Fraction Removed* = Fraction, $X$ of source mass at time $t_1$ that is removed by source remediation activities. This fraction is assumed to be the same for all components in the source zone. $0 \le X \le 1$

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

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

# Transport Parameters



Sigmav: 0.1

vMin: 0.5

vMax: 1.5

Number of Stream Tubes: 100

alphay (m): 0.5

alphaz (m): 0.1

*Sigmav* = Coefficient of variation for velocity field, equal to the ratio of the pore velocity standard deviation, divided by the mean pore velocity, $\sigma_v / \bar{v}$ . This results in a scale-dependent dispersivity that is equal to ½(*sigmav*)$^2 \bar{x}$ , where $\bar{x}$ is the average front location at a given time. A *sigmav* value of 0.1 results in a longitudinal dispersivity equal to 1/200 of the travel distance; a *sigmav* value of 0.44721 results in a longitudinal dispersivity equal to 1/10 of the travel distance. The table below gives Sigmav values corresponding to different longitudinal dispersivities:

| $\alpha_x$ | *Sigmav* |
|---|---|
| *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. Typically set equal to 0, except when very small *sigmav* 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.

*vMax* = maximum normalized streamtube velocity. Magnitude depends on *sigmav*. For small *sigmav* (~0.1), $v_{max}$~1.5. For moderate *sigmav* (~0.25), $v_{max}$~2.0. For large *sigmav* (~0.447), $v_{max}$~3.0.

*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 will still represent the dispersion reasonably well in many cases, but it will not be “smooth”. A solution calculated with 500 streamtubes will usually be smooth, 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*. A maximum of 10,000 streamtubes can be used.

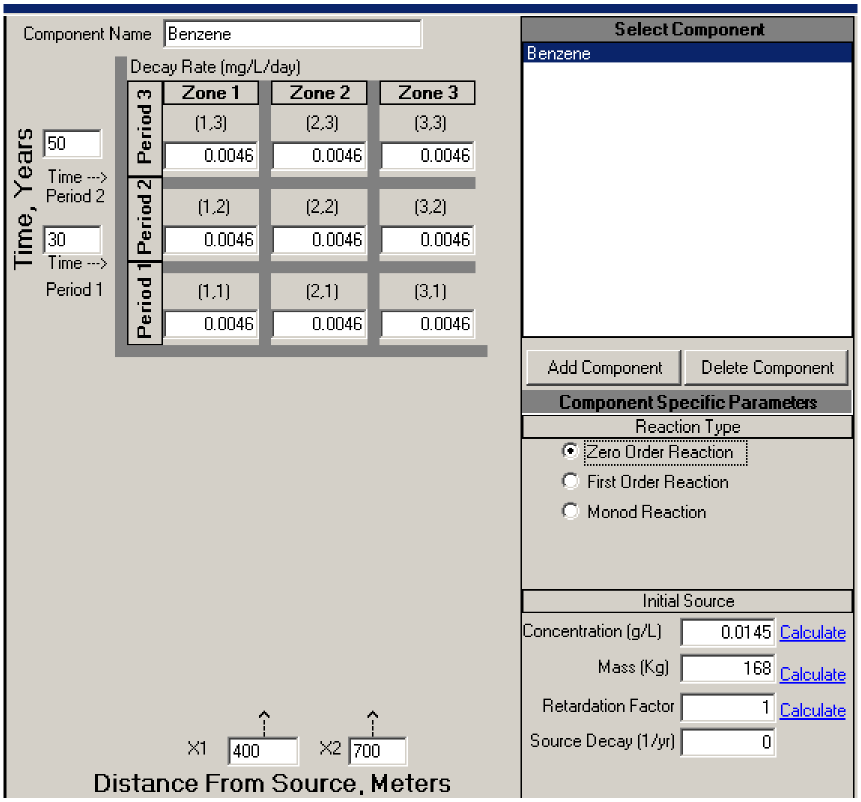
*alphay* = Transverse dispersivity, $\alpha_y$ , constant value in m. This is generally 1/10 or less of the effective longitudinal value. If a negative value is used, the transverse dispersivity is scale-dependent, with a value equal to the travel distance multiplied by the absolute value of alphay.

*alphaz* = Vertical dispersivity, $\alpha_z$ , constant value in m. This is generally 1/100 or less (perhaps much less) of the effective longitudinal value. If a negative value is used, the vertical dispersivity is scale-dependent, with a value equal to the travel distance multiplied by the absolute value of alphaz.

# Component Setup and Reaction

For each selected component, the user is allowed to set the initial source parameters (discussed above). The user can also select from three optional reaction types, zero order, first order or Monod's reaction. Each reaction type has its own reaction matrix which allows the user to specify three reaction zones in space as well as three reaction time periods. Below are example input screens for each reaction type for the component benzene:

Zero Order:



Component Name: Benzene

Decay Rate (mg/L/day)

| | Zone 1 | Zone 2 | Zone 3 |
|---|---|---|---|
| Period 3 | (1,3)<br>0.0046 | (2,3)<br>0.0046 | (3,3)<br>0.0046 |
| Period 2 | (1,2)<br>0.0046 | (2,2)<br>0.0046 | (3,2)<br>0.0046 |
| Period 1 | (1,1)<br>0.0046 | (2,1)<br>0.0046 | (3,1)<br>0.0046 |

Time, Years

50 Time ---> Period 2

30 Time ---> Period 1

X1 400 X2 700

Distance From Source, Meters

Select Component: Benzene

Component Specific Parameters

Reaction Type

● Zero Order Reaction

○ First Order Reaction

○ Monod Reaction

Initial Source

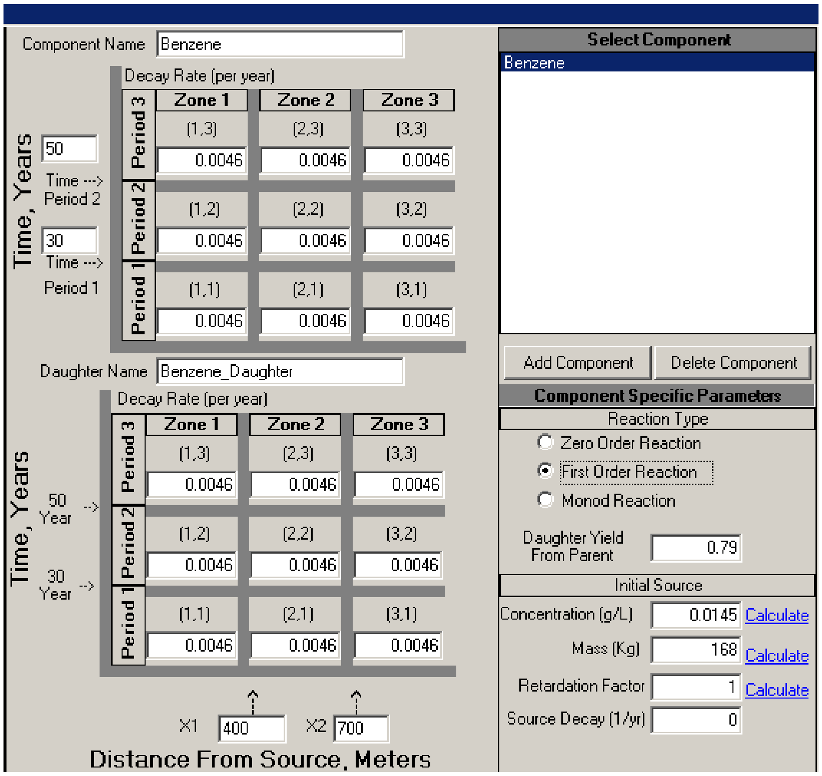
Concentration (g/L): 0.0145

Mass (Kg): 168

Retardation Factor: 1

Source Decay (1/yr): 0

First Order:



Component Name: Benzene

Decay Rate (per year)

| | Zone 1 | Zone 2 | Zone 3 |
|---|---|---|---|
| Period 3 | (1,3) 0.0046 | (2,3) 0.0046 | (3,3) 0.0046 |
| Period 2 | (1,2) 0.0046 | (2,2) 0.0046 | (3,2) 0.0046 |
| Period 1 | (1,1) 0.0046 | (2,1) 0.0046 | (3,1) 0.0046 |

Time ---> Period 2: 50

Time ---> Period 1: 30

Daughter Name: Benzene_Daughter

Decay Rate (per year)

| | Zone 1 | Zone 2 | Zone 3 |
|---|---|---|---|
| Period 3 | (1,3) 0.0046 | (2,3) 0.0046 | (3,3) 0.0046 |
| Period 2 | (1,2) 0.0046 | (2,2) 0.0046 | (3,2) 0.0046 |
| Period 1 | (1,1) 0.0046 | (2,1) 0.0046 | (3,1) 0.0046 |

50 Year -->

30 Year -->

X1: 400

X2: 700

Select Component: Benzene

Component Specific Parameters

Reaction Type

○ Zero Order Reaction

● First Order Reaction

○ Monod Reaction

Daughter Yield From Parent: 0.79

Initial Source

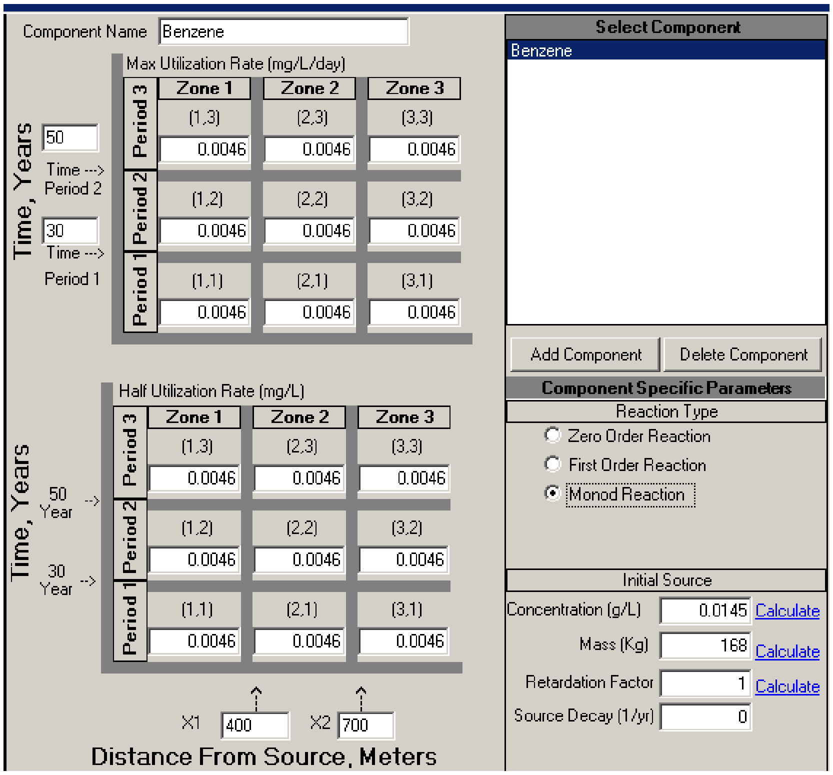
Concentration (g/L): 0.0145

Mass (Kg): 168

Retardation Factor: 1

Source Decay (1/yr): 0

Monod's Reaction:



Component Name: Benzene

Max Utilization Rate (mg/L/day)

| | Zone 1 | Zone 2 | Zone 3 |
|---|---|---|---|
| Period 3 | (1,3) 0.0046 | (2,3) 0.0046 | (3,3) 0.0046 |
| Period 2 | (1,2) 0.0046 | (2,2) 0.0046 | (3,2) 0.0046 |
| Period 1 | (1,1) 0.0046 | (2,1) 0.0046 | (3,1) 0.0046 |

Time ---> Period 2: 50

Time ---> Period 1: 30

Half Utilization Rate (mg/L)

| | Zone 1 | Zone 2 | Zone 3 |
|---|---|---|---|
| Period 3 | (1,3) 0.0046 | (2,3) 0.0046 | (3,3) 0.0046 |
| Period 2 | (1,2) 0.0046 | (2,2) 0.0046 | (3,2) 0.0046 |
| Period 1 | (1,1) 0.0046 | (2,1) 0.0046 | (3,1) 0.0046 |

50 Year -->

30 Year -->

X1: 400

X2: 700

Select Component: Benzene

Component Specific Parameters

Reaction Type

○ Zero Order Reaction

○ First Order Reaction

● Monod Reaction

Initial Source

Concentration (g/L): 0.0145

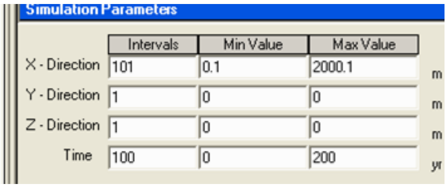
Mass (Kg): 168

Retardation Factor: 1

Source Decay (1/yr): 0

# Simulation Output Parameters

*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.



Simulation Parameters

| | Intervals | Min Value | Max Value | |
|---|---|---|---|---|
| X - Direction | 101 | 0.1 | 2000.1 | m |
| Y - Direction | 1 | 0 | 0 | m |
| Z - Direction | 1 | 0 | 0 | m |
| Time | 100 | 0 | 200 | yr |

*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 horizontal no flow boundary for dispersion; this location gives the maximum concentration at a given x-y location.

*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.

# REMFuel Tutorials

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## Tutorial 1

### Reactive Transport of BTEX and MTBE with Remediation

This problem involves a hypothetical release of BTEX and MTBE (gasoline spill) from an aqueous source zone (beneath a lens of product sitting on the water table). The source contains 5 LNAPL components (benzene, toluene, xylenes, ethylbenzene, and MTBE with TBA produced as a daughter product). The source concentrations reflect Raoult's law partitioning with typical gasoline compositions, and the source masses reflect a 5,000 gallon gasoline release. Aqueous phase biodegradation of the LNAPL compounds in the source zone is included for all components except MTBE. The source parameters are listed in the table below. This example problem makes use of all three biodegradation reaction mechanisms: Zero Order, First Order, and Monod kinetics.

| Component# | chemical | Mole fraction in gasoline | Pure aqueous solubility<br>g/l | Source zone aqueous decay rate 1/yr | Initial source mass, kg | Initial source concentration, g/L | Retardation factor |
|---|---|---|---|---|---|---|---|
| 1 | MTBE | .10 | 50. | 1.39 | 1500 | 5.00 | 1.0 |
| 2 | Benzene | .01 | 1.8 | .693 | 150 | 0.018 | 1.5 |
| 3 | Toluene | .05 | 0.5 | 1.39 | 750 | 0.025 | 2.0 |
| 4 | Xylenes | .1 | .2 | 1.39 | 1500 | 0.020 | 2.5 |
| 5 | Ethylbenzene | .02 | .2 | 1.39 | 300 | 0.004 | 2.0 |
| 1-daughter | TBA | 0 | - | - | - | - | 1.0 |

The source volume is 10m by 10m by 1m thick with a water flux of 20 m/yr. The components undergo various plume reactions and MTBE produces TBA as a daughter.

Source remediation occurs at year 10, with 90% removal of the remaining mass of all compounds. Plume remediation occurs from years 10 to 12, and the reaction rates are increased by a factor of 10 during this time.

Benzene, uses the Monod kinetics reaction, with $\mu_{max}$ = 0.01 mg/L/d and $K_c$ = 2 mg/L.

Toluene uses the Monod kinetics reaction, with $\mu_{max}$ = 0.01 mg/L/d and $K_c$ =.01 mg/L.

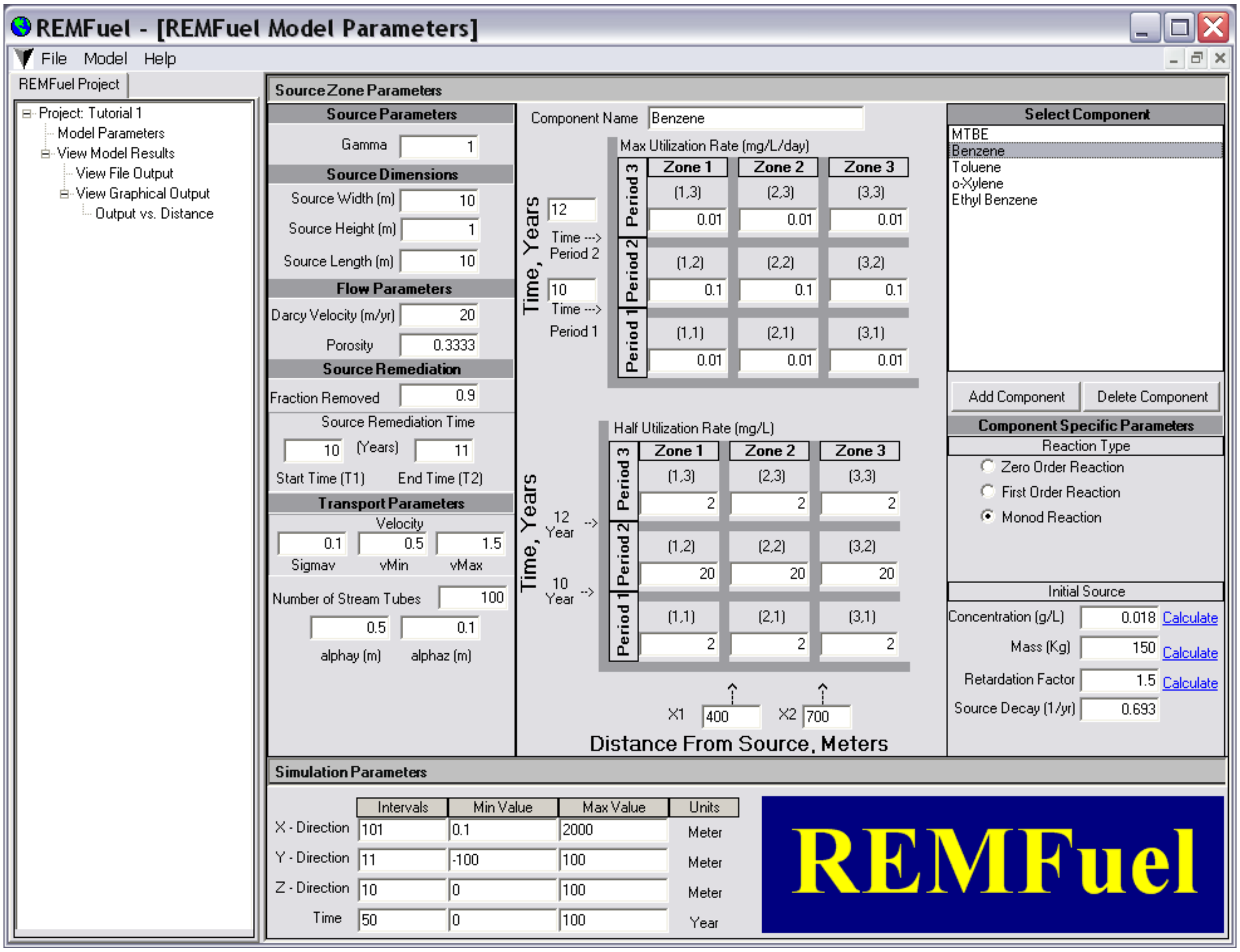
Xylenes (represented in this tutorial by o-Xylene), uses the Monod kinetics reaction, with $\mu_{max}$ = 0.01 mg/L/d and $K_c$ = 1000 mg/L.

Ethylbenzene uses the zero order reaction with a rate constant of $\gamma$ = 0.01 mg/L/d.

MTBE uses the first order reaction with a rate constant of $k$ = 0.0365/yr, and it produces TBA, which is given the same reaction rate.

The following are the *Model Parameters* screens for each component:

Benzene:



Source Zone Parameters

Source Parameters

Gamma 1

Source Dimensions

Source Width (m) 10

Source Height (m) 1

Source Length (m) 10

Flow Parameters

Darcy Velocity (m/yr) 20

Porosity 0.3333

Source Remediation

Fraction Removed 0.9

Source Remediation Time

10 (Years) 11

Start Time (T1) End Time (T2)

Transport Parameters

Velocity

| Sigmav | vMin | vMax |
|---|---|---|
| 0.1 | 0.5 | 1.5 |

Number of Stream Tubes 100

| alphay (m) | alphaz (m) |
|---|---|
| 0.5 | 0.1 |

Component Name Benzene

Max Utilization Rate (mg/L/day)

Time, Years: 12 Time ---> Period 2; 10 Time ---> Period 1

| | Zone 1 | Zone 2 | Zone 3 |
|---|---|---|---|
| Period 3 | (1,3)<br>0.01 | (2,3)<br>0.01 | (3,3)<br>0.01 |
| Period 2 | (1,2)<br>0.1 | (2,2)<br>0.1 | (3,2)<br>0.1 |
| Period 1 | (1,1)<br>0.01 | (2,1)<br>0.01 | (3,1)<br>0.01 |

Half Utilization Rate (mg/L)

Time, Years: 12 Year -->; 10 Year -->

| | Zone 1 | Zone 2 | Zone 3 |
|---|---|---|---|
| Period 3 | (1,3)<br>2 | (2,3)<br>2 | (3,3)<br>2 |
| Period 2 | (1,2)<br>20 | (2,2)<br>20 | (3,2)<br>20 |
| Period 1 | (1,1)<br>2 | (2,1)<br>2 | (3,1)<br>2 |

X1 400 X2 700

Distance From Source, Meters

Select Component

MTBE
Benzene
Toluene
o-Xylene
Ethyl Benzene

Component Specific Parameters

Reaction Type

○ Zero Order Reaction
○ First Order Reaction
● Monod Reaction

Initial Source

Concentration (g/L) 0.018

Mass (Kg) 150

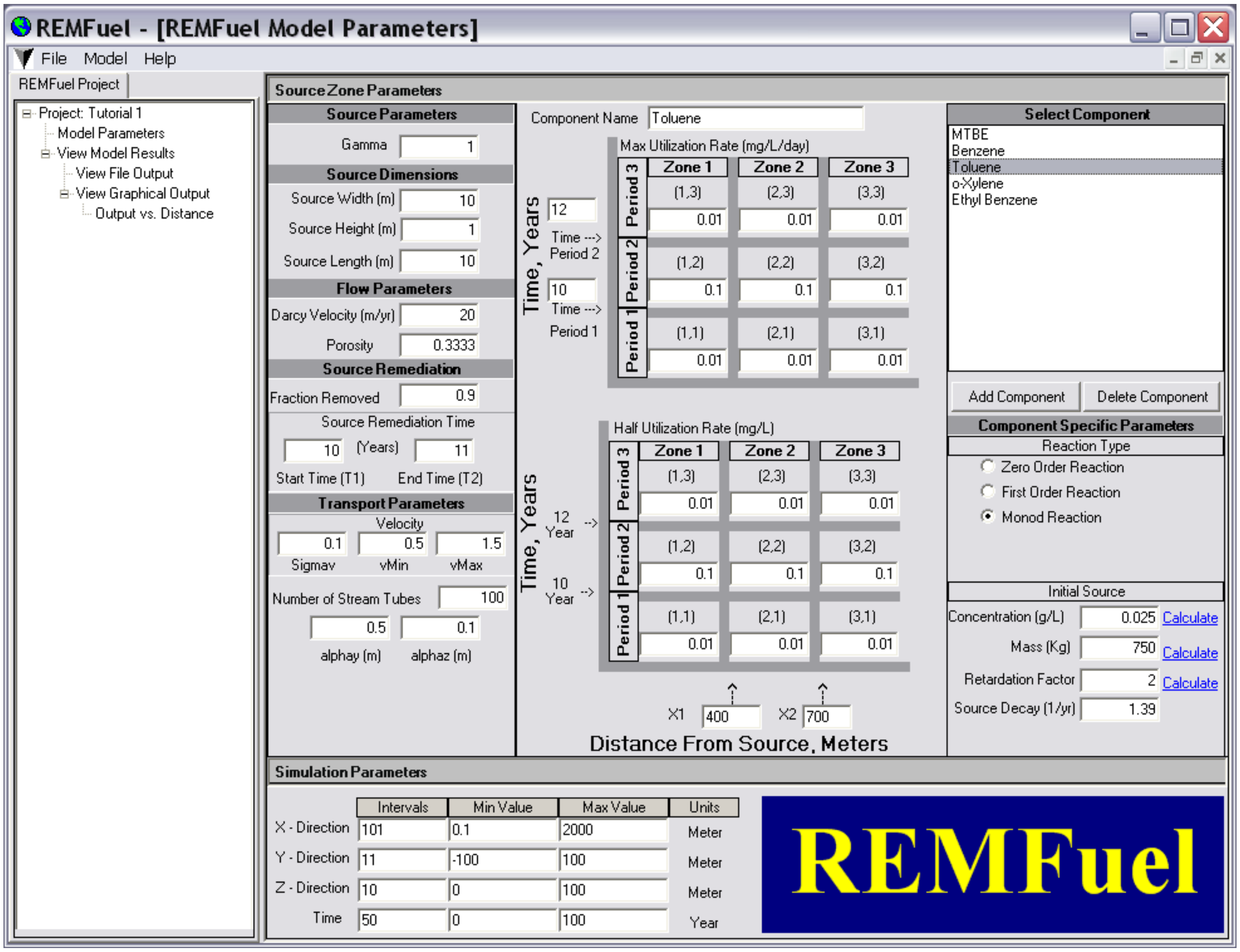
Retardation Factor 1.5

Source Decay (1/yr) 0.693

Simulation Parameters

| | Intervals | Min Value | Max Value | Units |
|---|---|---|---|---|
| X - Direction | 101 | 0.1 | 2000 | Meter |
| Y - Direction | 11 | -100 | 100 | Meter |
| Z - Direction | 10 | 0 | 100 | Meter |
| Time | 50 | 0 | 100 | Year |

Toluene:



**Source Zone Parameters**

**Source Parameters**

Gamma: 1

**Source Dimensions**

Source Width (m): 10

Source Height (m): 1

Source Length (m): 10

**Flow Parameters**

Darcy Velocity (m/yr): 20

Porosity: 0.3333

**Source Remediation**

Fraction Removed: 0.9

Source Remediation Time (Years): Start Time (T1) 10, End Time (T2) 11

**Transport Parameters**

Velocity: Sigmav 0.1, vMin 0.5, vMax 1.5

Number of Stream Tubes: 100

alphay (m): 0.5, alphaz (m): 0.1

Component Name: Toluene

Max Utilization Rate (mg/L/day)

Time, Years: Time --> Period 2: 12; Time --> Period 1: 10

| | Zone 1 | Zone 2 | Zone 3 |
|---|---|---|---|
| Period 3 | (1,3) 0.01 | (2,3) 0.01 | (3,3) 0.01 |
| Period 2 | (1,2) 0.1 | (2,2) 0.1 | (3,2) 0.1 |
| Period 1 | (1,1) 0.01 | (2,1) 0.01 | (3,1) 0.01 |

Half Utilization Rate (mg/L)

Time, Years: 12 Year -->; 10 Year -->

| | Zone 1 | Zone 2 | Zone 3 |
|---|---|---|---|
| Period 3 | (1,3) 0.01 | (2,3) 0.01 | (3,3) 0.01 |
| Period 2 | (1,2) 0.1 | (2,2) 0.1 | (3,2) 0.1 |
| Period 1 | (1,1) 0.01 | (2,1) 0.01 | (3,1) 0.01 |

X1: 400 X2: 700

Distance From Source, Meters

**Select Component**

MTBE
Benzene
Toluene
o-Xylene
Ethyl Benzene

**Component Specific Parameters**

Reaction Type

○ Zero Order Reaction
○ First Order Reaction
● Monod Reaction

Initial Source

Concentration (g/L): 0.025

Mass (Kg): 750

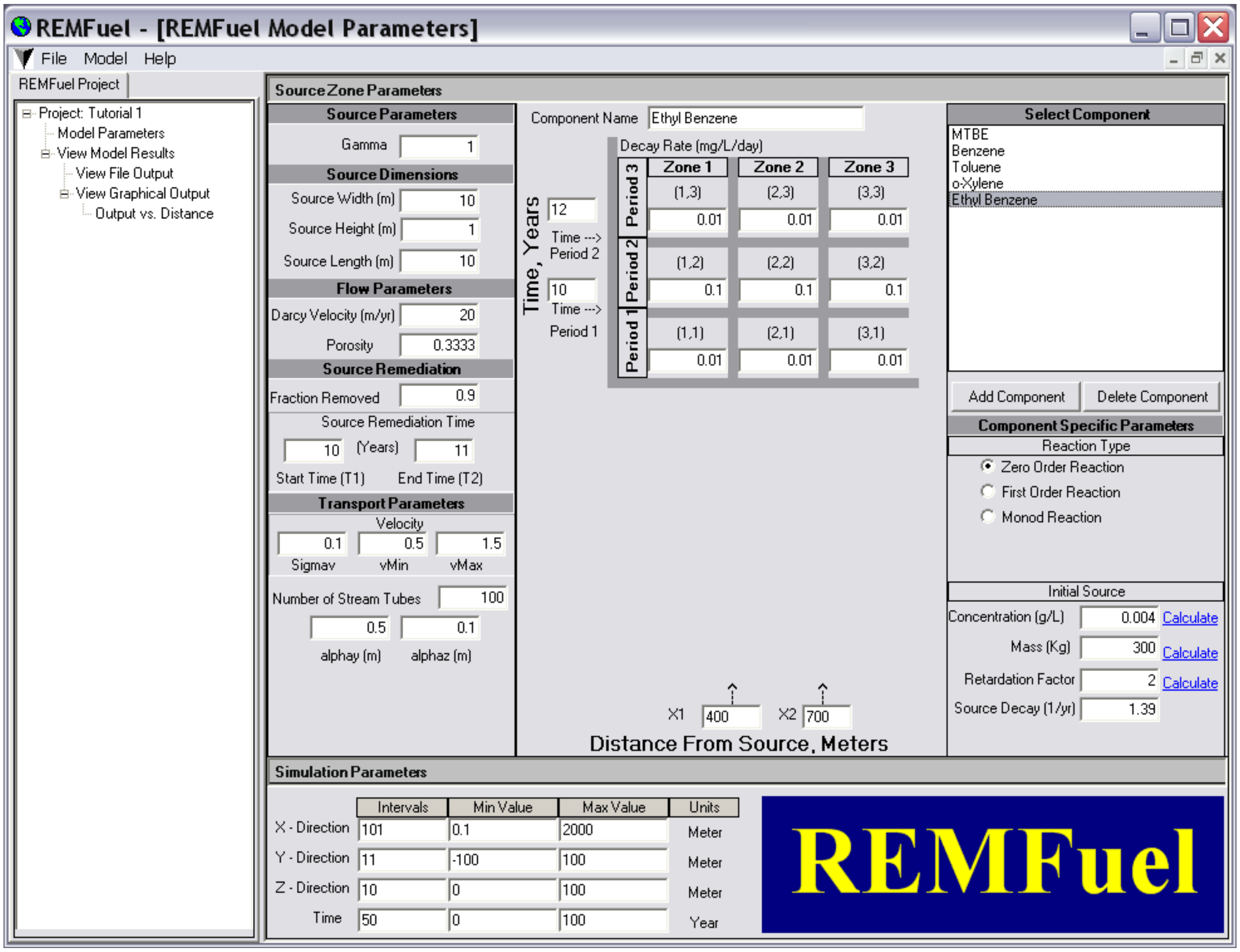
Retardation Factor: 2

Source Decay (1/yr): 1.39

**Simulation Parameters**

| | Intervals | Min Value | Max Value | Units |
|---|---|---|---|---|
| X - Direction | 101 | 0.1 | 2000 | Meter |
| Y - Direction | 11 | -100 | 100 | Meter |
| Z - Direction | 10 | 0 | 100 | Meter |
| Time | 50 | 0 | 100 | Year |

Ethyl Benzene:



**Source Zone Parameters**

**Source Parameters**

Gamma 1

**Source Dimensions**

Source Width (m) 10
Source Height (m) 1
Source Length (m) 10

**Flow Parameters**

Darcy Velocity (m/yr) 20
Porosity 0.3333

**Source Remediation**

Fraction Removed 0.9

Source Remediation Time
Start Time (T1) 10 (Years) End Time (T2) 11

**Transport Parameters**

Velocity
Sigmav 0.1
vMin 0.5
vMax 1.5

Number of Stream Tubes 100
alphay (m) 0.5
alphaz (m) 0.1

Component Name Ethyl Benzene

Decay Rate (mg/L/day)

|  | Zone 1 | Zone 2 | Zone 3 |
|---|---|---|---|
| Period 3 | (1,3) 0.01 | (2,3) 0.01 | (3,3) 0.01 |
| Period 2 | (1,2) 0.1 | (2,2) 0.1 | (3,2) 0.1 |
| Period 1 | (1,1) 0.01 | (2,1) 0.01 | (3,1) 0.01 |

Time, Years
12 Time ---> Period 2
10 Time ---> Period 1

X1 400
X2 700
Distance From Source, Meters

**Select Component**

MTBE
Benzene
Toluene
o-Xylene
Ethyl Benzene

**Component Specific Parameters**

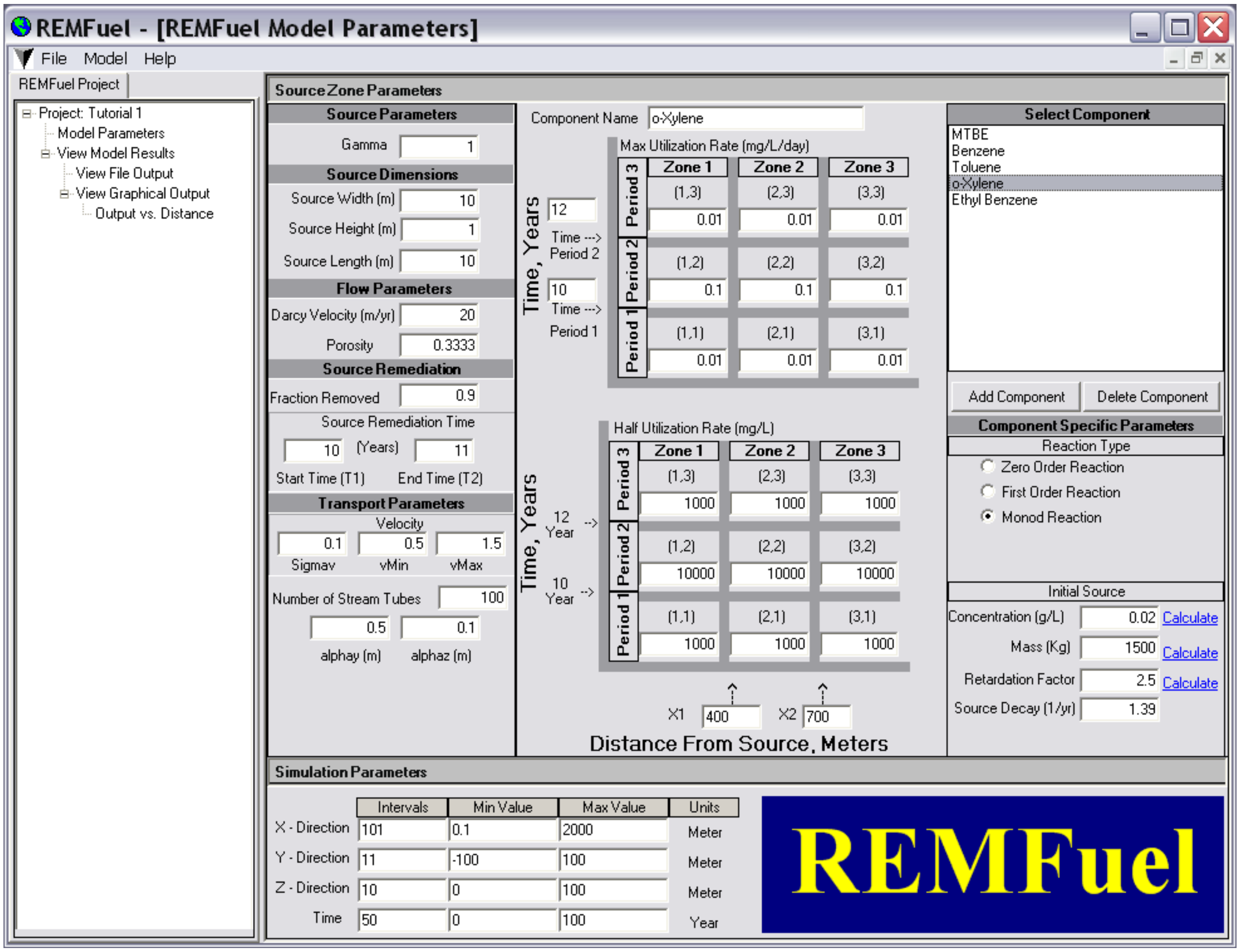
Reaction Type
● Zero Order Reaction
○ First Order Reaction
○ Monod Reaction

Initial Source
Concentration (g/L) 0.004
Mass (Kg) 300
Retardation Factor 2
Source Decay (1/yr) 1.39

**Simulation Parameters**

|  | Intervals | Min Value | Max Value | Units |
|---|---|---|---|---|
| X - Direction | 101 | 0.1 | 2000 | Meter |
| Y - Direction | 11 | -100 | 100 | Meter |
| Z - Direction | 10 | 0 | 100 | Meter |
| Time | 50 | 0 | 100 | Year |

Xylenes (represented by o-Xylene):



**Source Parameters**

Gamma 1

**Source Dimensions**

Source Width (m) 10
Source Height (m) 1
Source Length (m) 10

**Flow Parameters**

Darcy Velocity (m/yr) 20
Porosity 0.3333

**Source Remediation**

Fraction Removed 0.9
Source Remediation Time: Start Time (T1) 10 (Years) End Time (T2) 11

**Transport Parameters**

Velocity: Sigmav 0.1, vMin 0.5, vMax 1.5
Number of Stream Tubes 100
alphay (m) 0.5, alphaz (m) 0.1

Component Name o-Xylene

Max Utilization Rate (mg/L/day)

Time --> Period 2: 12
Time --> Period 1: 10

| | Zone 1 | Zone 2 | Zone 3 |
|---|---|---|---|
| Period 3 | (1,3) 0.01 | (2,3) 0.01 | (3,3) 0.01 |
| Period 2 | (1,2) 0.1 | (2,2) 0.1 | (3,2) 0.1 |
| Period 1 | (1,1) 0.01 | (2,1) 0.01 | (3,1) 0.01 |

Half Utilization Rate (mg/L)

12 Year -->
10 Year -->

| | Zone 1 | Zone 2 | Zone 3 |
|---|---|---|---|
| Period 3 | (1,3) 1000 | (2,3) 1000 | (3,3) 1000 |
| Period 2 | (1,2) 10000 | (2,2) 10000 | (3,2) 10000 |
| Period 1 | (1,1) 1000 | (2,1) 1000 | (3,1) 1000 |

X1 400
X2 700

**Select Component**

- MTBE
- Benzene
- Toluene
- o-Xylene
- Ethyl Benzene

**Component Specific Parameters**

Reaction Type

○ Zero Order Reaction
○ First Order Reaction
● Monod Reaction

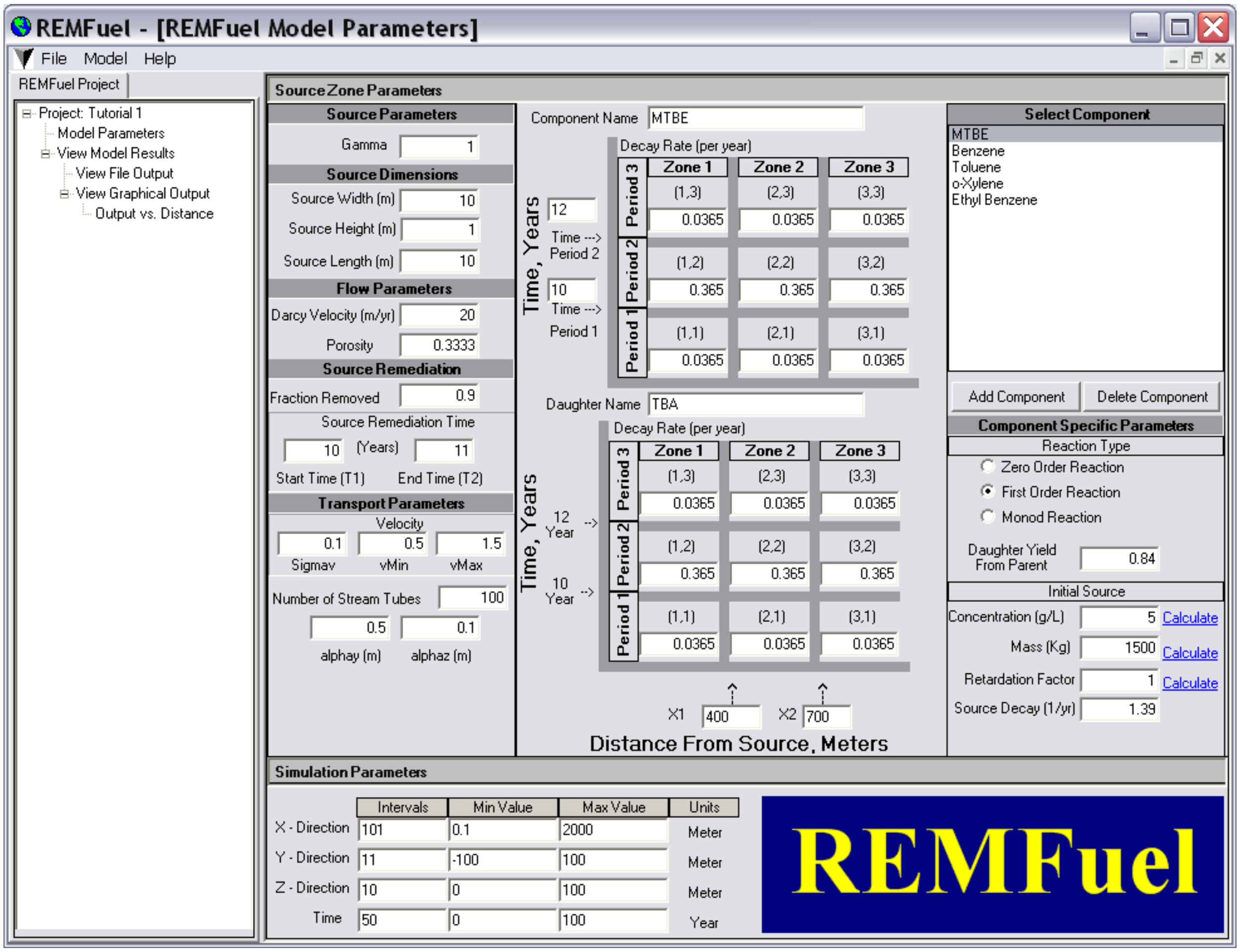
Initial Source

Concentration (g/L) 0.02
Mass (Kg) 1500
Retardation Factor 2.5
Source Decay (1/yr) 1.39

**Simulation Parameters**

| | Intervals | Min Value | Max Value | Units |
|---|---|---|---|---|
| X - Direction | 101 | 0.1 | 2000 | Meter |
| Y - Direction | 11 | -100 | 100 | Meter |
| Z - Direction | 10 | 0 | 100 | Meter |
| Time | 50 | 0 | 100 | Year |

MTBE:



**Source Parameters**

Gamma: 1

**Source Dimensions**

Source Width (m): 10
Source Height (m): 1
Source Length (m): 10

**Flow Parameters**

Darcy Velocity (m/yr): 20
Porosity: 0.3333

**Source Remediation**

Fraction Removed: 0.9
Source Remediation Time: 10 (Years) 11
Start Time (T1): 10
End Time (T2): 11

**Transport Parameters**

Velocity: Sigmav 0.1, vMin 0.5, vMax 1.5
Number of Stream Tubes: 100
alphay (m): 0.5
alphaz (m): 0.1

Component Name: MTBE

Decay Rate (per year)

Time, Years: 12 Time ---> Period 2; 10 Time ---> Period 1

| | Zone 1 | Zone 2 | Zone 3 |
|---|---|---|---|
| Period 3 | (1,3) 0.0365 | (2,3) 0.0365 | (3,3) 0.0365 |
| Period 2 | (1,2) 0.365 | (2,2) 0.365 | (3,2) 0.365 |
| Period 1 | (1,1) 0.0365 | (2,1) 0.0365 | (3,1) 0.0365 |

Daughter Name: TBA

Decay Rate (per year)

Time, Years: 12 Year -->; 10 Year -->

| | Zone 1 | Zone 2 | Zone 3 |
|---|---|---|---|
| Period 3 | (1,3) 0.0365 | (2,3) 0.0365 | (3,3) 0.0365 |
| Period 2 | (1,2) 0.365 | (2,2) 0.365 | (3,2) 0.365 |
| Period 1 | (1,1) 0.0365 | (2,1) 0.0365 | (3,1) 0.0365 |

X1: 400
X2: 700

Distance From Source, Meters

**Select Component**

MTBE
Benzene
Toluene
o-Xylene
Ethyl Benzene

**Component Specific Parameters**

Reaction Type
○ Zero Order Reaction
● First Order Reaction
○ Monod Reaction

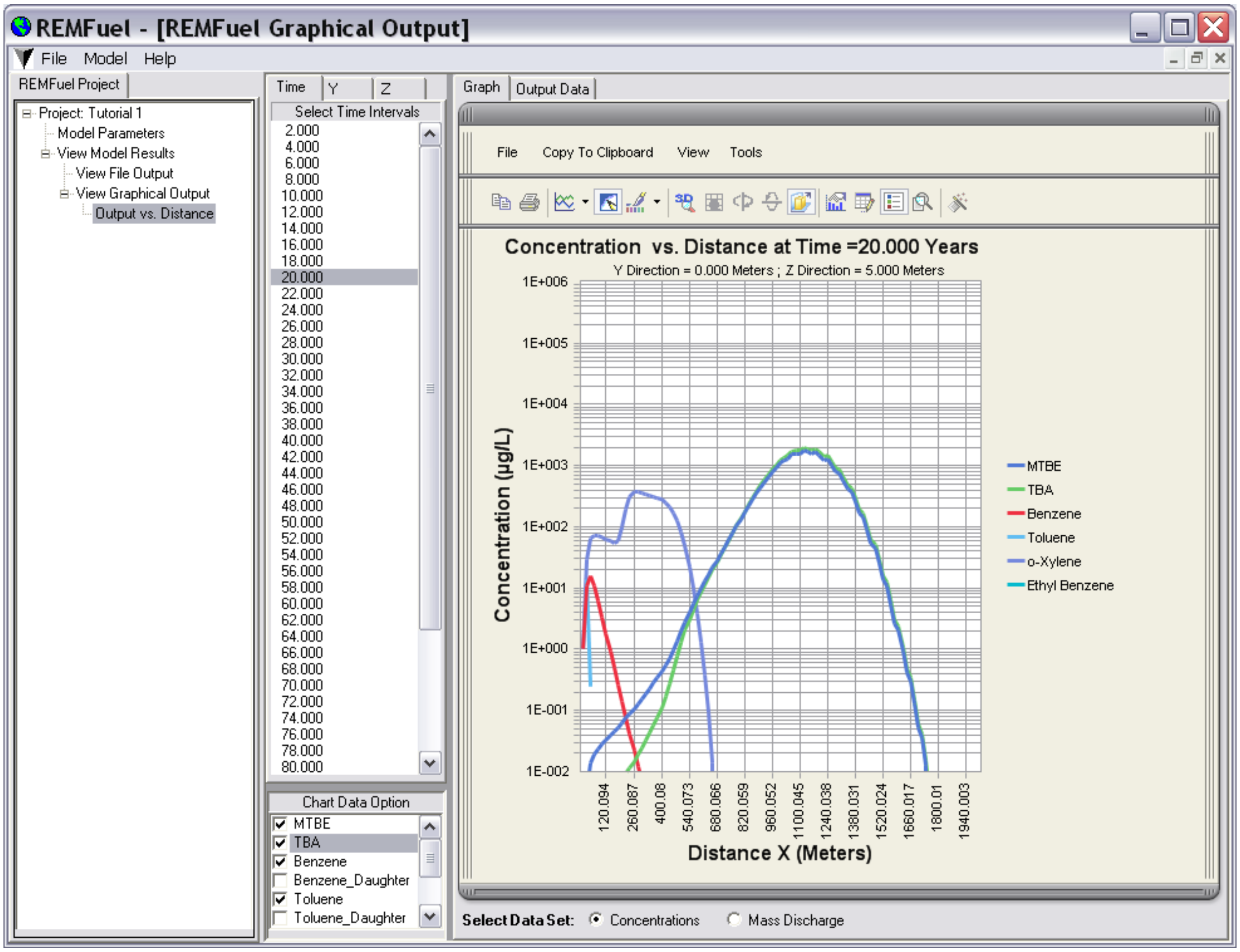
Daughter Yield From Parent: 0.84

Initial Source
Concentration (g/L): 5
Mass (Kg): 1500
Retardation Factor: 1
Source Decay (1/yr): 1.39

**Simulation Parameters**

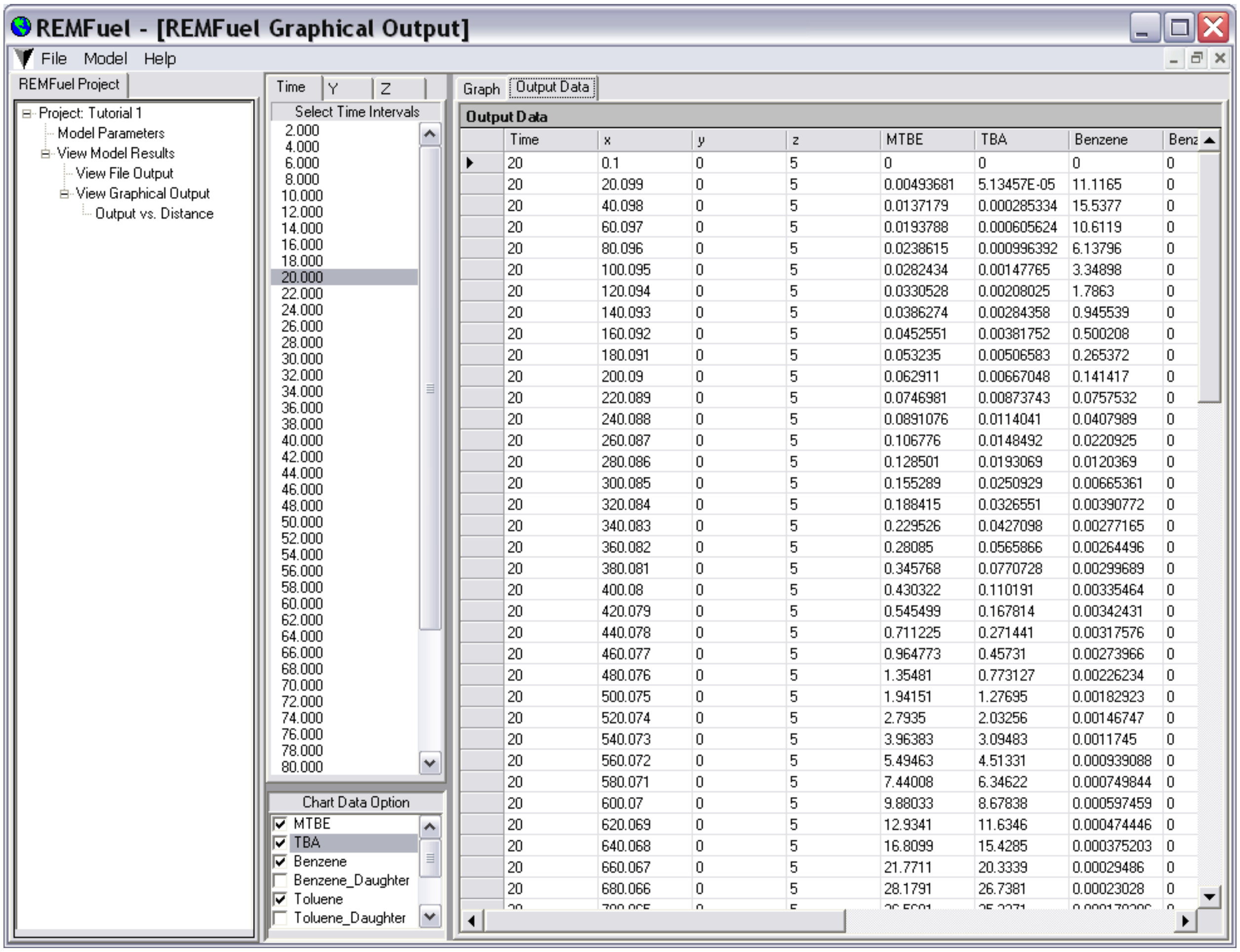
| | Intervals | Min Value | Max Value | Units |
|---|---|---|---|---|
| X - Direction | 101 | 0.1 | 2000 | Meter |
| Y - Direction | 11 | -100 | 100 | Meter |
| Z - Direction | 10 | 0 | 100 | Meter |
| Time | 50 | 0 | 100 | Year |

The concentration profiles after 20 years are plotted below for this problem.



From this screen, the modeler can vary the concentration profile in space and time using the “Y” and “Z” tabs next to “Time”.

Clicking on the “Output Data” tab brings up the current concentration profile as columns of raw data:



Output Data

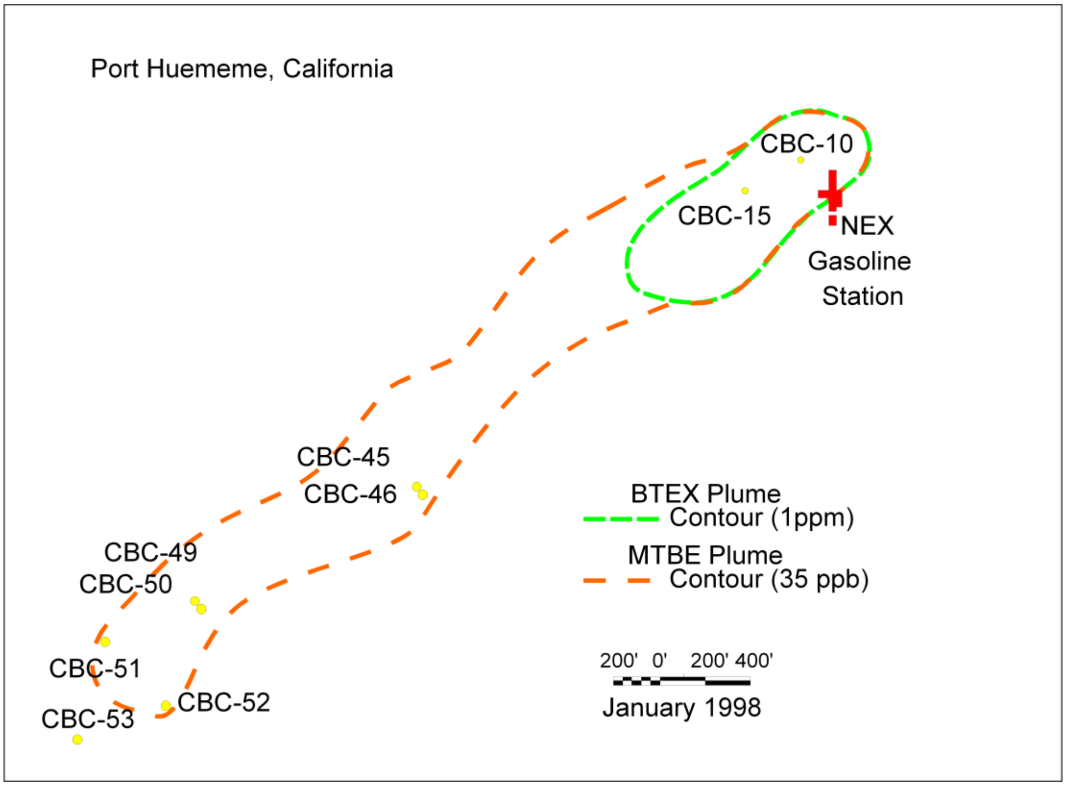
| Time | x | y | z | MTBE | TBA | Benzene | Benz |
|---|---|---|---|---|---|---|---|
| 20 | 0.1 | 0 | 5 | 0 | 0 | 0 | 0 |
| 20 | 20.099 | 0 | 5 | 0.00493681 | 5.13457E-05 | 11.1165 | 0 |
| 20 | 40.098 | 0 | 5 | 0.0137179 | 0.000285334 | 15.5377 | 0 |
| 20 | 60.097 | 0 | 5 | 0.0193788 | 0.000605624 | 10.6119 | 0 |
| 20 | 80.096 | 0 | 5 | 0.0238615 | 0.000996392 | 6.13796 | 0 |
| 20 | 100.095 | 0 | 5 | 0.0282434 | 0.00147765 | 3.34898 | 0 |
| 20 | 120.094 | 0 | 5 | 0.0330528 | 0.00208025 | 1.7863 | 0 |
| 20 | 140.093 | 0 | 5 | 0.0386274 | 0.00284358 | 0.945539 | 0 |
| 20 | 160.092 | 0 | 5 | 0.0452551 | 0.00381752 | 0.500208 | 0 |
| 20 | 180.091 | 0 | 5 | 0.053235 | 0.00506583 | 0.265372 | 0 |
| 20 | 200.09 | 0 | 5 | 0.062911 | 0.00667048 | 0.141417 | 0 |
| 20 | 220.089 | 0 | 5 | 0.0746981 | 0.00873743 | 0.0757532 | 0 |
| 20 | 240.088 | 0 | 5 | 0.0891076 | 0.0114041 | 0.0407989 | 0 |
| 20 | 260.087 | 0 | 5 | 0.106776 | 0.0148492 | 0.0220925 | 0 |
| 20 | 280.086 | 0 | 5 | 0.128501 | 0.0193069 | 0.0120369 | 0 |
| 20 | 300.085 | 0 | 5 | 0.155289 | 0.0250929 | 0.00665361 | 0 |
| 20 | 320.084 | 0 | 5 | 0.188415 | 0.0326551 | 0.00390772 | 0 |
| 20 | 340.083 | 0 | 5 | 0.229526 | 0.0427098 | 0.00277165 | 0 |
| 20 | 360.082 | 0 | 5 | 0.28085 | 0.0565866 | 0.00264496 | 0 |
| 20 | 380.081 | 0 | 5 | 0.345768 | 0.0770728 | 0.00299689 | 0 |
| 20 | 400.08 | 0 | 5 | 0.430322 | 0.110191 | 0.00335464 | 0 |
| 20 | 420.079 | 0 | 5 | 0.545499 | 0.167814 | 0.00342431 | 0 |
| 20 | 440.078 | 0 | 5 | 0.711225 | 0.271441 | 0.00317576 | 0 |
| 20 | 460.077 | 0 | 5 | 0.964773 | 0.45731 | 0.00273966 | 0 |
| 20 | 480.076 | 0 | 5 | 1.35481 | 0.773127 | 0.00226234 | 0 |
| 20 | 500.075 | 0 | 5 | 1.94151 | 1.27695 | 0.00182923 | 0 |
| 20 | 520.074 | 0 | 5 | 2.7935 | 2.03256 | 0.00146747 | 0 |
| 20 | 540.073 | 0 | 5 | 3.96383 | 3.09483 | 0.0011745 | 0 |
| 20 | 560.072 | 0 | 5 | 5.49463 | 4.51331 | 0.000939088 | 0 |
| 20 | 580.071 | 0 | 5 | 7.44008 | 6.34622 | 0.000749844 | 0 |
| 20 | 600.07 | 0 | 5 | 9.88033 | 8.67838 | 0.000597459 | 0 |
| 20 | 620.069 | 0 | 5 | 12.9341 | 11.6346 | 0.000474446 | 0 |
| 20 | 640.068 | 0 | 5 | 16.8099 | 15.4285 | 0.000375203 | 0 |
| 20 | 660.067 | 0 | 5 | 21.7711 | 20.3339 | 0.00029486 | 0 |
| 20 | 680.066 | 0 | 5 | 28.1791 | 26.7381 | 0.00023028 | 0 |

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

## Reactive Transport of MTBE from a Gasoline Spill Site

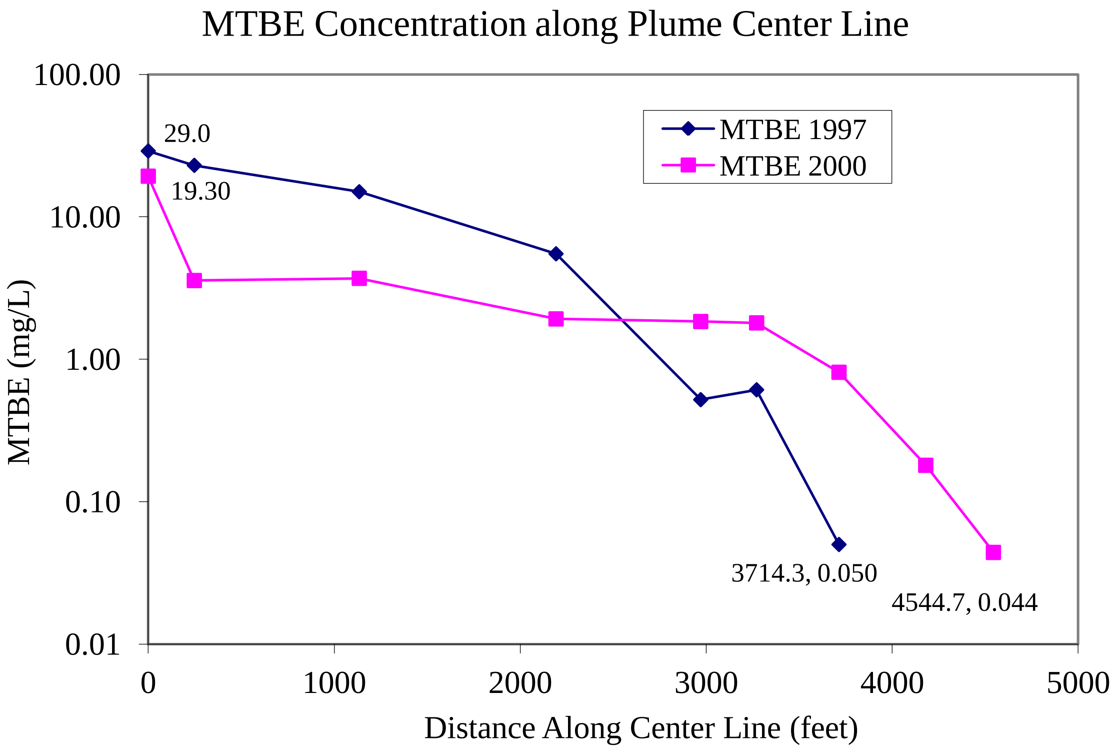
This tutorial is based on one of the most famous dissolved MTBE plumes in the United States located in Port Hueneme, CA. Several thousand gallons of gasoline containing MTBE was released at the NEX gasoline station on the site in 1984-85. As a result, a large plume of MTBE and a relatively small plume of BTEX compounds were found at the site (see the following figure).



The dissolved MTBE plume here is very long because there is only limited biodegradation occurring in the initial period following the spill. The dissolved benzene plume extends only a short distance from the source, however, indicating the occurrence of biodegradation of BTEX in groundwater.

Source Calibration for MTBE:

The size of the NAPL source as measured from the presence of NAPL at the water table is 150×100×1 m (L×W×H). The source parameters to be calibrated are Gamma, source concentration at the time of release ($C_0$), initial source mass ($M_0$), and source decay rate ($\lambda_s$). The following figure shows the MTBE concentration in 1997 and 2000 (before any remediation activity), that is, after 12 and 15 years from release, respectively.

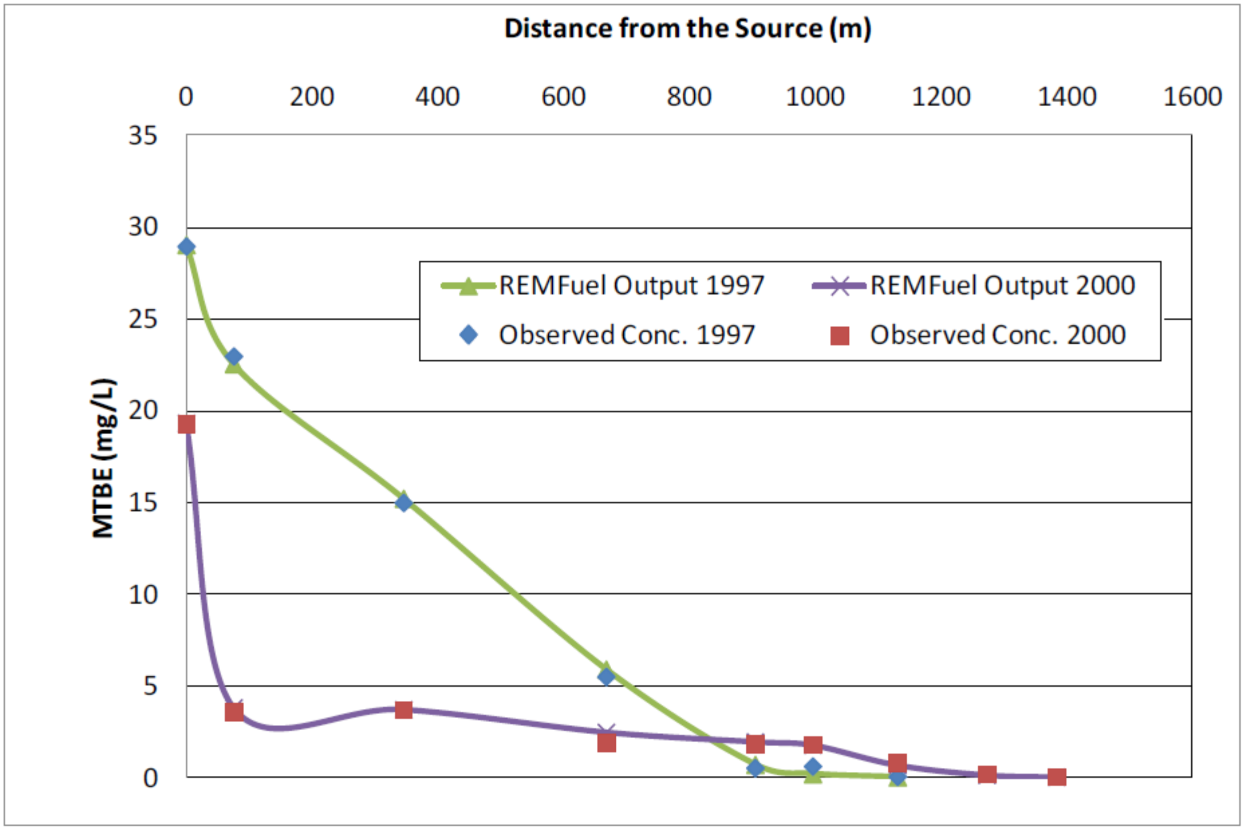


From the above figure, calibration targets for the source concentrations were 29 and 19.3 mg/L at 12 and 15 years from release, respectively.
Since the source was not completely depleted in 15 years, the Gamma value should be equal or greater than 1.0 (see Figures 3 and 4 of the user's manual). For gasoline with high MTBE, the initial source concentration was calibrated to be 0.15 g/L. For Gamma value of 1.0 and a release of 6,800 gal gasoline (equivalent to 2,210 Kg of MTBE) and source decay rate of 0.10 yr$^{-1}$, the calibrated concentrations at 12 and 15 years (that is, in 1997 and 2000) were 29.08 and 19.34 mg/L, respectively. Note that the calculated value of source decay rate assuming exponential decay between 1997 and 2000 is 0.136 yr$^{-1}$.

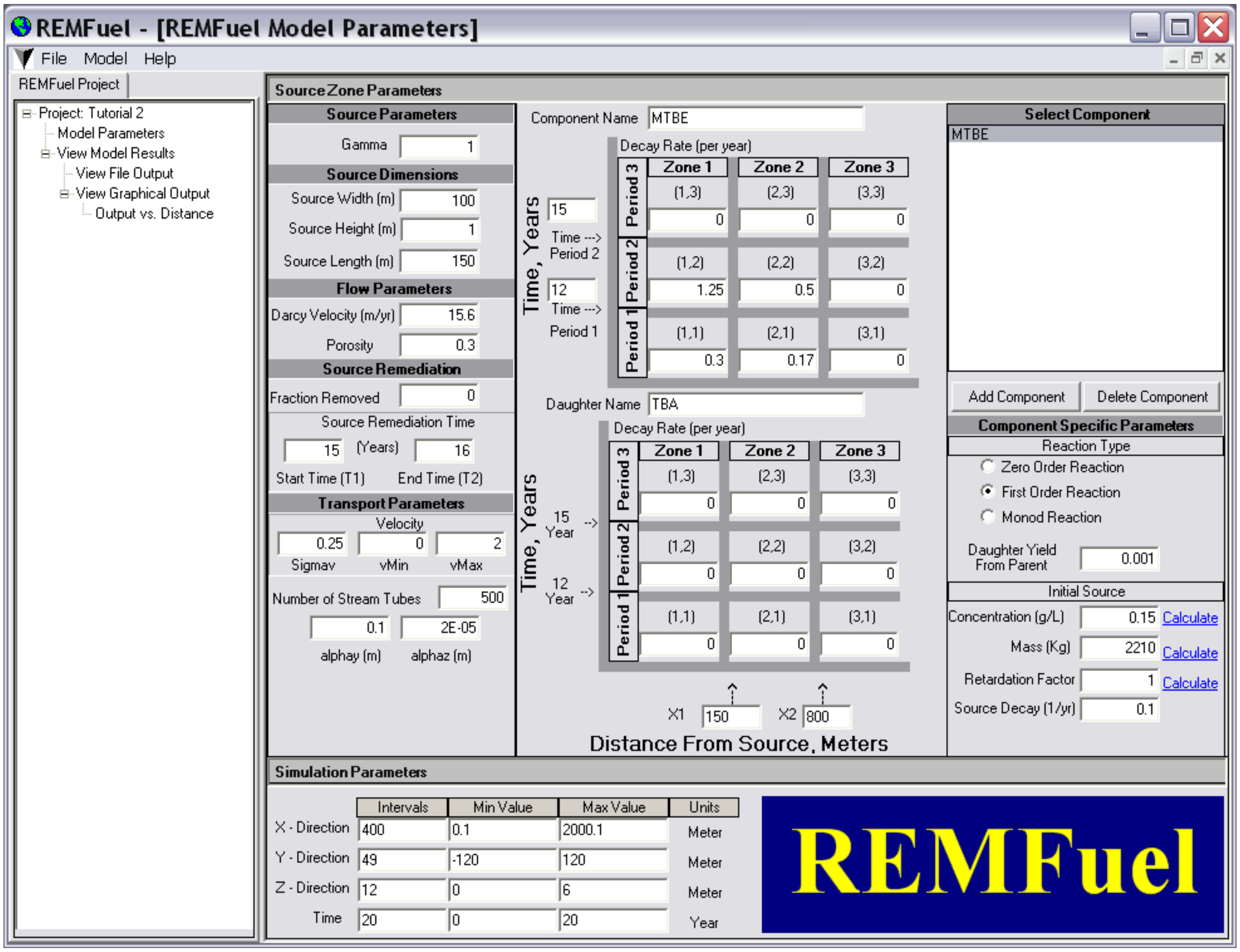
Plume Calibration for MTBE:
The figure above also shows that the length of the 50 ug/L plume in 1997 was 3710 ft (~1130 m) and the plume expanded to about 4540 ft (~1385 m) in 2000. These concentrations were used as calibration targets for the MTBE plume. Also, a sharp decline in MTBE concentration near the source is visible for the 2000 data. The same zone in the 1997 data shows a consistent decline in concentration. This shows that the MTBE concentration degraded near the source, where the BTEX plume was present. Because of this sharp decline, a greater value for decay rate was assumed for Zone 1 between time periods 1 and 2. Zone 2 was assumed to be between 150 and 800 m (i.e., apx.500 to 2600 ft), since the MTBE concentration is much flatter in this area. Zone 3 shows sharp decline due to dispersion at the front edge of the plume.

Darcy velocity and porosity of the aquifer were 15.6 m/yr and 0.3, respectively. The longitudinal dispersion was calibrated by assuming *Sigmav* to be 0.25 and vMax to be 2 (=1 + 4× *Sigmav*), which is equivalent to a longitudinal dispersivity of 1/50th of the plume length (see the 'Model Input Variables' section in the manual for detail). The lateral extent of the plume was between 160 and 170 m, which could be achieved by assuming the lateral dispersivity to be 0.1 m. Vertical spreading of the plume was in the 2 m range, which calibrates to 0.00002 m vertical dispersivity.

Following figures show model calibration chart and REMFuel's input and output screenshots for the calibrated model.



Model Inputs:



Source Zone Parameters

Source Parameters
Gamma 1

Source Dimensions
Source Width (m) 100
Source Height (m) 1
Source Length (m) 150

Flow Parameters
Darcy Velocity (m/yr) 15.6
Porosity 0.3

Source Remediation
Fraction Removed 0
Source Remediation Time
Start Time (T1) 15 (Years) End Time (T2) 16

Transport Parameters
Velocity
Sigmav 0.25
vMin 0
vMax 2
Number of Stream Tubes 500
alphay (m) 0.1
alphaz (m) 2E-05

Component Name MTBE

Decay Rate (per year)

| | Zone 1 | Zone 2 | Zone 3 |
|---|---|---|---|
| Period 3 | (1,3) 0 | (2,3) 0 | (3,3) 0 |
| Period 2 | (1,2) 1.25 | (2,2) 0.5 | (3,2) 0 |
| Period 1 | (1,1) 0.3 | (2,1) 0.17 | (3,1) 0 |

Time, Years
15 Time ---> Period 2
12 Time ---> Period 1

Daughter Name TBA

Decay Rate (per year)

| | Zone 1 | Zone 2 | Zone 3 |
|---|---|---|---|
| Period 3 | (1,3) 0 | (2,3) 0 | (3,3) 0 |
| Period 2 | (1,2) 0 | (2,2) 0 | (3,2) 0 |
| Period 1 | (1,1) 0 | (2,1) 0 | (3,1) 0 |

Time, Years
15 Year -->
12 Year -->

X1 150 X2 800
Distance From Source, Meters

Select Component
MTBE

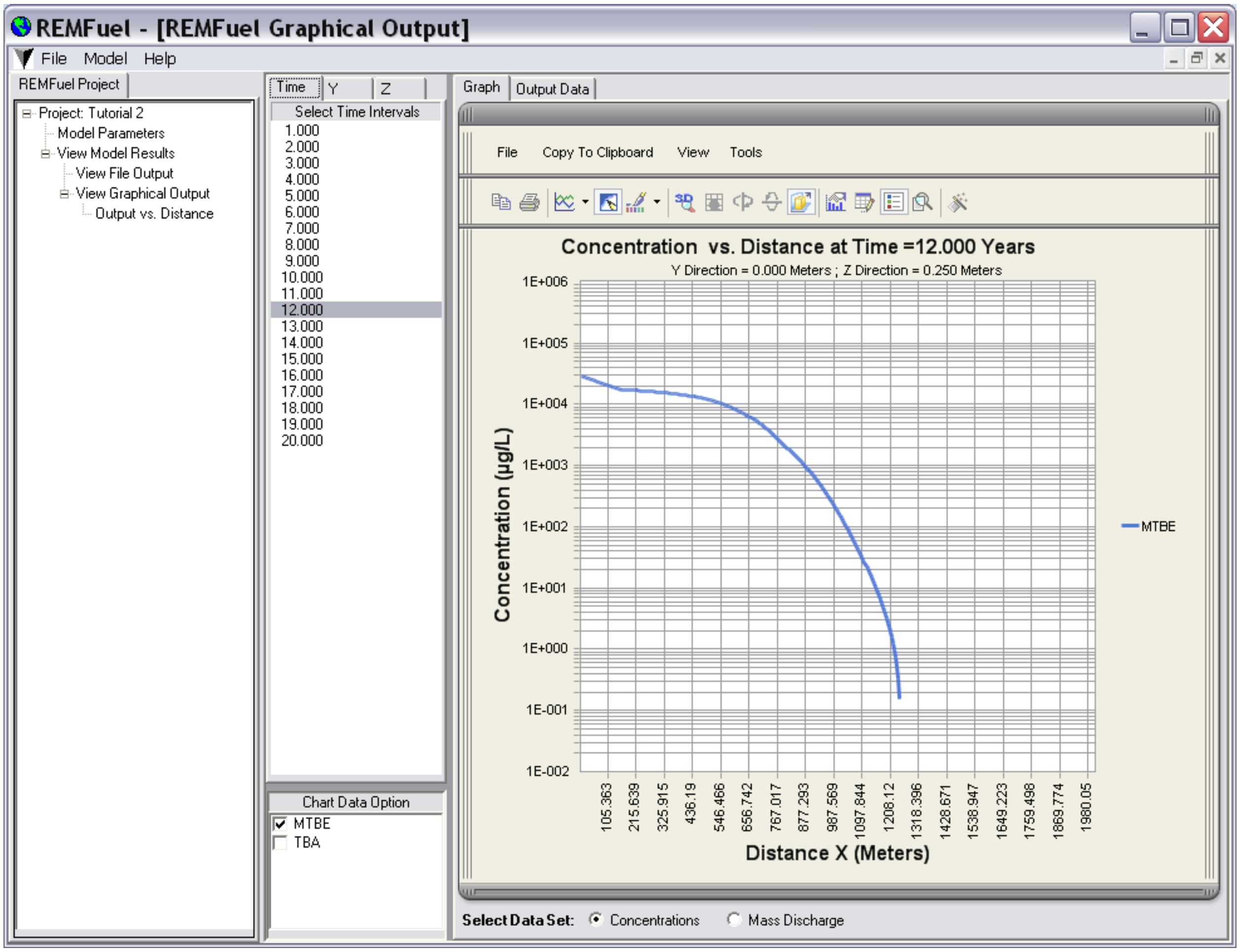
Component Specific Parameters
Reaction Type
○ Zero Order Reaction
● First Order Reaction
○ Monod Reaction
Daughter Yield From Parent 0.001

Initial Source
Concentration (g/L) 0.15
Mass (Kg) 2210
Retardation Factor 1
Source Decay (1/yr) 0.1

Simulation Parameters

| | Intervals | Min Value | Max Value | Units |
|---|---|---|---|---|
| X - Direction | 400 | 0.1 | 2000.1 | Meter |
| Y - Direction | 49 | -120 | 120 | Meter |
| Z - Direction | 12 | 0 | 6 | Meter |
| Time | 20 | 0 | 20 | Year |

The concentration profile after 12 years:

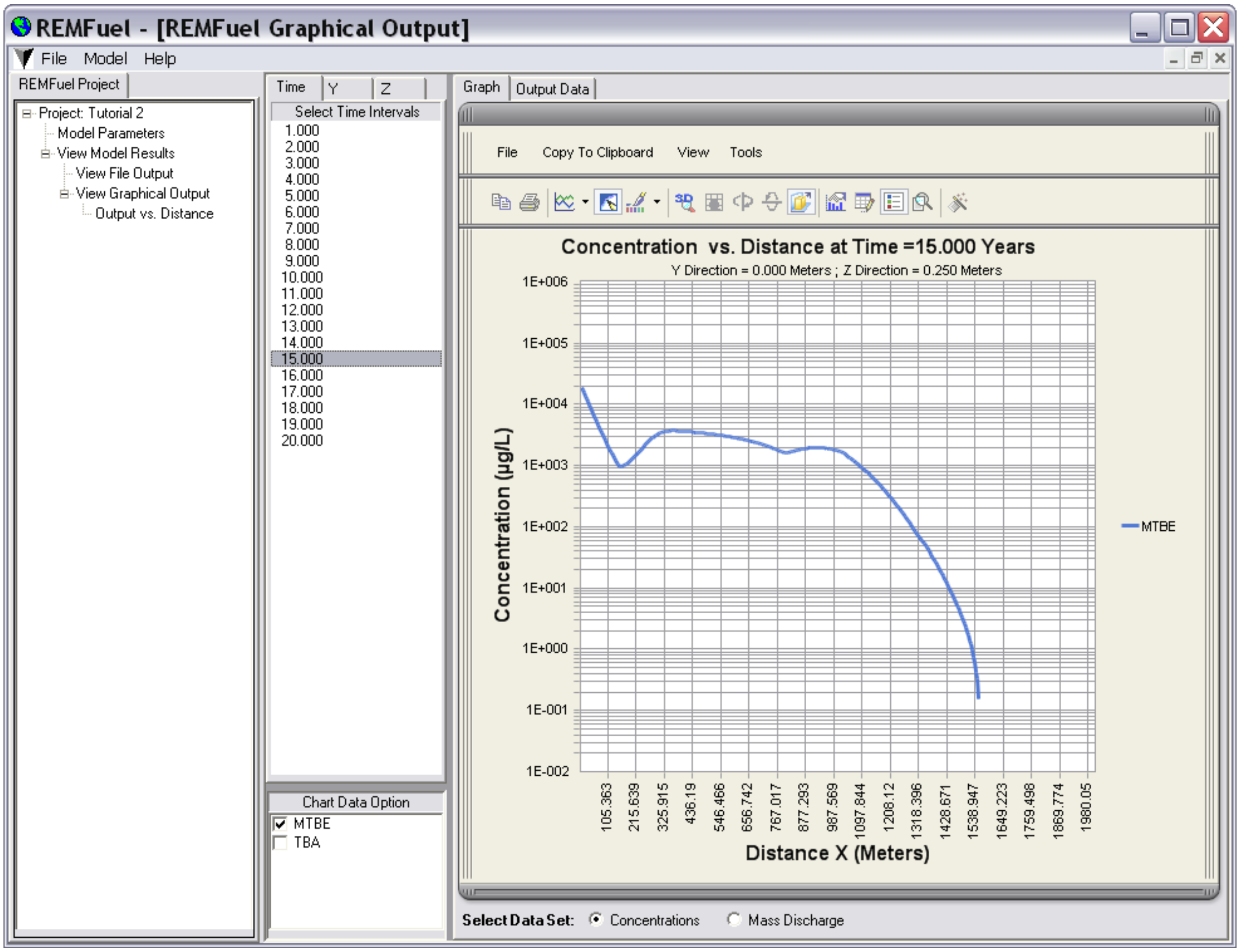


Time: 12.000

Chart Data Option: ☑ MTBE ☐ TBA

**Select Data Set:** ● Concentrations ○ Mass Discharge

The concentration profile after 15 years:



☑ MTBE
☐ TBA

**Select Data Set:** ● Concentrations ○ Mass Discharge

# References

Abramowitz, M. and I.A. Stegun, Eds. (1972), *Handbook of Mathematical Functions*, Dover Publications, Inc., New York, NY.

Aziz, C.E., C.J. Newell, J.R. Gonzales, P. Hass, T.P. Clement, and Y. Sun (2000), BIOCHLOR Natural Attenuation Decision Support System User's Manual Version 1.0, EPA/600/R-00/008, U.S. EPA National Risk Management Research Laboratory, Cincinnati, OH.

Aziz, C.E., C.J. Newell, and J.R. Gonzales (2002), BIOCHLOR Natural Attenuation Decision Support System Version 2.2 User's Manual Addendum, http://www.epa.gov/ada/download/models/biochlor22.pdf.

Charbeneau, R.J. (2000), *Groundwater Hydraulics and Pollutant Transport*, Prentice Hall, Upper Saddle River, NJ, 593 p.

Chen, N.H. (1983), *Process Reactor Design*, Allyn and Bacon, Inc., Boston, MA, 545 p.

Chen, W., A.T. Kan, C.J. Newell, E. Moore, and M.B. Tomson. (2002), More realistic soil cleanup standards with dual-equilibrium desorption, *Ground Water,* Vol. 40, No. 2, 153-164.

Cleary, R.W., and M.J. Ungs (1978), Groundwater pollution and hydrology, mathematical models and computer programs, Rep. 78-WR-15, Water Resources Program, Princeton University, Princeton, NJ.

Domenico, P.A. (1987), An analytical model for multidimensional transport of a decaying contaminant species, *Journal of Hydrology*, Vol. 91, 49-58.

Domenico, P.A., and F.W. Schwartz (1990), *Physical and Chemical Hydrogeology*, Wiley, New York, NY.

Falta, R.W. (2008), Methodology for comparing source and plume remediation alternatives, *Ground Water*, Vol. 46, No. 2, 272-285.

Falta, R.W., P.S.C. Rao, and N. Basu (2005a), Assessing the impacts of partial mass depletion in DNAPL source zones: I. Analytical modeling of source strength functions and plume response, *Journal of Contaminant Hydrology*, Vol. 78, No. 4, 259-280.

Falta, R.W., N. Basu, and P.S.C. Rao (2005b), Assessing the impacts of partial mass depletion in DNAPL source zones: II. Coupling source strength functions to plume evolution, *Journal of Contaminant Hydrology*. Vol. 79, No. 1-2, 45-66.

Fure, A.D., J.W. Jawitz, and M.D. Annable (2006), DNAPL source depletion: Linking architecture and flux response, *Journal of Contaminant Hydrology*, Vol. 85, No. 3–4, 118–140.

Greve, R.M. (2007), A Post-Closure Assessment of Natural Attenuation at Eight Leaking Underground Storage Tank Sites. M.S. Thesis, University of Wisconsin, Madison, WI, 167 p.

Huntley, D. and G.D. Beckett (2002), Persistence of LNAPL sources: relationship between risk reduction and LNAPL recovery, *Journal of Contaminant Hydrology*, Vol. 59, 3-26.

Javandel, I., C. Doughty, and C.F. Tsang (1984), *Groundwater Transport: Handbook of Mathematical Models,* American Geophysical Union Water Resources Monograph 10, Washington, DC.

Jawitz, J.W., A.D. Fure, G.G. Demmy, S. Berglund, and P.S.C. Rao (2005), Groundwater contaminant flux reduction resulting from nonaqueous phase liquid mass reduction, *Water Resources Research*, Vol. 41, No.10, W10408.

Johnson, P.C., P.D. Lundegard, and Z. Liu (2006a), Source zone natural attenuation at petroleum hydrocarbon spill sites— I: Site-specific assessment approach, *Ground Water Monitoring & Remediation*, Vol. 26, No. 4, 82–92.

Lewandowski, G. and G. Mortimer (2003), Estimation of anaerobic biodegradation rate constants at MGP sites, *Ground Water*, Vol. 42, No. 3, 433-437.

Lundegard, P.D., and P.C. Johnson (2006b), Source zone natural attenuation at petroleum hydrocarbon spill sites—II: Application to a former oil field, *Ground Water Monitoring & Remediation*, Vol. 26, No. 4, 93–106.

McGuire, T.M., J.M. McDade, and C.J. Newell (2006), Performance of DNAPL source depletion technologies at 59 chlorinated solvent-impacted sites, *Ground Water Monitoring & Remediation*, Vol. 26, No. 1, p. 73-84.

Mormile, M.R., Liu, S. and J.M. Suflita (1994), Anaerobic biodegradation of gasoline oxygenates: Extrapolation of information to multiple sites and redox conditions, *Environmental Science & Technology*, Vol. 28, 1727-1732.

Newell, C.J., and D.T. Adamson (2005), Planning-level source decay models to evaluate impact of source depletion on remediation time frame, *Remediation*, Autumn 2005, 27-47.

Newell, C.J., R.K. McLeod, and J.R. Gonzales (1996), BIOSCREEN Natural Attenuation Decision Support System User’s Manual Version 1.3, EPA/600/R-96/087, U.S. EPA National Risk Management Research Laboratory, Cincinnati, OH.

Newell, C.J., I. Cowie, T.M. McGuire, and W. McNab (2006), Multi-year temporal changes in chlorinated solvent concentrations at 23 MNA sites, *Journal of Environmental Engineering*, Vol. 132, No. 6, 653-663.

Ostendorf, D.W., and D.H. Kampbell (1991), Biodegradation of hydrocarbon vapors in the unsaturated zone, *Water Resources Research*, Vol. 27, No. 4, 453-462.

Park, E., and J.C. Parker (2005), Evaluation of an upscale model for DNAPL dissolution kinetics in heterogeneous aquifers, *Advances in Water Research*, Vol. 26, No. 12, 1280-1291.

Parker, J.C, and E. Park (2004), Modeling field-scale dense nonaqueous phase liquid dissolution kinetics in heterogeneous aquifers, *Water Resources Research*, Vol. 40, W05109, 12 pp.

Parker, J.C., and R.W. Falta (2008), Comparison of alternative upscaled model formulations for simulating DNAPL source dissolution and biodecay, *Advances in Water Resources*, Vol. 31, 1325-1332.

Potter, T.L., and K.E. Simmons (1998), Composition of petroleum mixtures, Total Petroleum Hydrocarbon Criteria Working Group Series, Vol. 2, University of Massachusetts, Amherst, MA.

Rao, P.S.C. and J.W. Jawitz (2003), Comment on “Steady-state mass transfer from single-component dense non-aqueous phase liquids in uniform flow fields” by T.C. Sale & D.B. McWhorter, *Water Resources Research*, 39, No. 3, 1-3.

Rao, P.S.C., J.W. Jawitz, C.G. Enfield, R. Falta, M.D. Annabel, and A.L.Wood (2001), Technology integration for contaminated site remediation: Cleanup goals and performance metrics. pp. 410-412, *Ground Water Quality*, Sheffield, UK.

Reinhard, M., G.D. Hopkins, E. Steinle-Darling, and C.A. LeBron (2005), In situ biotransformation of BTEX compounds under methanogenic conditions, *Ground Water Monitoring & Remediation*, Vol. 25, No. 4, 50-59.

Small, M.C. (2003), Managing the Risks of Exposure to Methyl Tertiary Butyl Ether (MTBE) Contamination in Ground Water at Leaking Underground Storage Tank (LUST) Sites, Ph.D. thesis, University of California, Berkeley.

Somsamak, P., H.H. Richnow, and M.M. Haggblom (2005), Carbon isotope fractionation during anaerobic biotransformation of methyl tert-butyl ether and tert-amyl methyl ether, *Environmental Science & Technology*, Vol. 39, No. 1, 103-109.

Srinivasan, V., T.P. Clement, and K.K. Lee (2007), Domenico solution – Is it valid? *Ground Water*, Vol. 45, No. 2, 136-146.

Suarez, M.P., and H.S. Rifai (1999), Biodegradation rates for fuel hydrocarbons and chlorinated solvents in groundwater, *Bioremediation Journal*, Vol. 3, No. 4, 337-362.

van Genuchten, M.T., and W.J. Alves (1982), Analytical Solutions of the One-Dimensional Convection-Dispersive Solute Transport Equation, U.S. Department of Agriculture, Technical Bulletin No. 1661, 151 p.

Weaver, J.W., L. Jordan, and D.B. Hall (2005), Predicted Ground Water, Soil and Soil Gas Impacts from US Gasolines, 2004 First Analysis of the Autumnal Data, U.S. Environmental Protection Agency, Washington, DC, EPA 600/R-05/032.

Weaver, J.W., L. R. Exum, and L.M. Prieto (2010), Gasoline Composition Regulations Affecting LUST Sites, EPA/600/R-10/001, U.S. Environmental Protection Agency, Washington, DC.

West, M.R., B.H. Kueper, and M.J. Ungs (2007), On the use and error of approximation in the Domenico (1987) solution, *Ground Water*, Vol. 45, No. 2, 126-135.

Wexler, E.J. (1992), Analytical Solutions for One-, Two-, and Three-Dimensional Solute Transport in Ground-Water Systems with Uniform Flow, Techniques of Water-Resources Investigations of the United States Geological Survey, Chapter B7, Book 3, *Applications of Hydraulics,* U.S. Government Printing Office, 190 p.

Wilson, J.T. and C. Adair (2007), Monitored Natural Attenuation of Tertiary Butyl Alcohol (TBA) in Ground Water at Gasoline Spill Sites, EPA/600/R-07/100, U.S. Environmental Protection Agency, Cincinnati, OH.

Wilson, J.T., P.M. Kaiser, and C. Adair (2005), Monitored Natural Attenuation of MTBE as a Risk Management Option at Leaking Underground Storage Tank Sites, EPA/600/R‑04/179, U.S. Environmental Protection Agency, Cincinnati, OH.

Wilson, J.T., K. Banks, R.C. Earle, Y. He, T. Kuder, and C. Adair (2008), Natural Attenuation of the Lead Scavengers and 1,2-Dichloroethane (1,2-DCA) at Motor Fuel Release Sites and Implications for Risk Management, EPA 600/R-08/107, U.S. Environmental Protection Agency, Cincinnati, OH.

Zhu, J., and J.F. Sykes (2004), Simple screening models of NAPL dissolution in the subsurface, *Journal of Contaminant Hydrology*, Vol. 72, 245-258.