# SourceDK

**Remediation Timeframe
Decision Support System**

USER'S MANUAL

Version 1.0
April, 2004

By

S.K. Farhat, Ph.D., P.C. de Blanc, Ph.D., P.E., and C.J. Newell, Ph.D., P.E., DEE
Groundwater Services, Inc.
Houston, Texas

James R. Gonzales and Jesse Perez
Technology Transfer Division
Air Force Center for Environmental Excellence
Brooks AFB, Texas

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SourceDK
REMEDIATION TIMEFRAME
DECISION SUPPORT SYSTEM

**AIR FORCE CENTER FOR ENVIRONMENTAL
EXCELLENCE TECHNOLOGY
TRANSFER DIVISION**

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INTRODUCTION

The need for source lifetime information is becoming more and more important to site managers. For example, the Environmental Protection Agency's (EPA) Monitored Natural Attenuation (MNA) Directive (EPA, 1999) states that:

> *"Once site characterization data have been collected and a conceptual model developed, the next step is to evaluate the potential efficacy of MNA as a remedial alternative. This involves collection of site-specific data sufficient to estimate with an acceptable level of confidence both the rate of attenuation processes and the anticipated time required to achieve remediation objectives."*

and

> *"…. determination of the most appropriate timeframe is achieved through a comparison of estimates of remediation timeframe for **all** appropriate remedy alternatives."*

and

> *"Furthermore, EPA expects that documenting the level of confidence on attenuation rates will provide more technically defensible predictions of remedial timeframes and form the basis for more effective performance monitoring programs."*

To help site managers estimate remediation timeframes and to understand the uncertainty in those estimates, the Technology Transfer Division of the U.S. Air Force Center for Environmental Excellence (AFCEE) has funded the development of a computerized source attenuation decision support system, SourceDK. The software is a screening-level tool that can be applied to a variety of different types of source zones in groundwater.

SourceDK is a planning-level screening model for estimating groundwater remediation timeframes and the uncertainties associated with the estimated timeframe. In this document, "remediation timeframe" is the time required for the high-concentration source zones at a site to reach a certain target concentration. While SourceDK is primarily geared for natural attenuation processes, it can also be used to estimate source lifetimes for some flushing-based technologies, primarily groundwater pump-and-treat.

The software, programmed in the Microsoft® Excel spreadsheet environment, gives the user different approaches or Tiers. From easiest to most complex, the three tiers are:

> **Tier 1 – Extrapolation:** Source zones that have extended records of concentration vs. time can be analyzed using the Tier 1 extrapolation tool. With this tool, log concentration vs. time is plotted and then extrapolated to estimate how long it will take to achieve a cleanup goal, assuming the current trend continues. This tool also provides the 90% and 95% confidence level in this estimate of the time to achieve the cleanup goal.

> **Tier 2 – Box Model:** In this tier, the simple box model developed for the BIOSCREEN model (Newell *et al.*, 1996) has been enhanced to include source mass estimation software and other features. The box model estimates source attenuation from a source mass estimate, the mass flux of constituents leaving the source zone, and biodegradation processes in the source zone. The uncertainty in the source lifetime estimate is also provided.

> **Tier 3 – Process Models:** This tier employs more detailed fundamental process-based equations to determine the time and amount of naturally flowing groundwater required to flush out dissolved-phase and NAPL dominated constituents from the source zone.

SourceDK was developed for the Air Force Center for Environmental Excellence Technology Transfer Division at Brooks Air Force Base, San Antonio, Texas by Groundwater Services, Inc., Houston, Texas.

INTENDED USES FOR SourceDK AND LIMITATIONS

SourceDK attempts to answer the following fundamental questions regarding MNA:

What is the remediation timeframe required to achieve groundwater clean-up goals?
What is the uncertainty in the remediation timeframe estimates?

> SourceDK uses three relatively simple approaches to estimate remediation timeframes and the uncertainty in the timeframe estimate. The model can be used to predict concentrations of dissolved constituents in groundwater over time at a particular well or particular zone at a site. The modeling approach is designed to account for the presence of non-aqueous phase liquids (NAPLs) and other source materials in the saturated zone which control how long organic groundwater plumes will persist in the subsurface. All three approaches include methods to estimate the uncertainty in any remediation timeframe estimate.
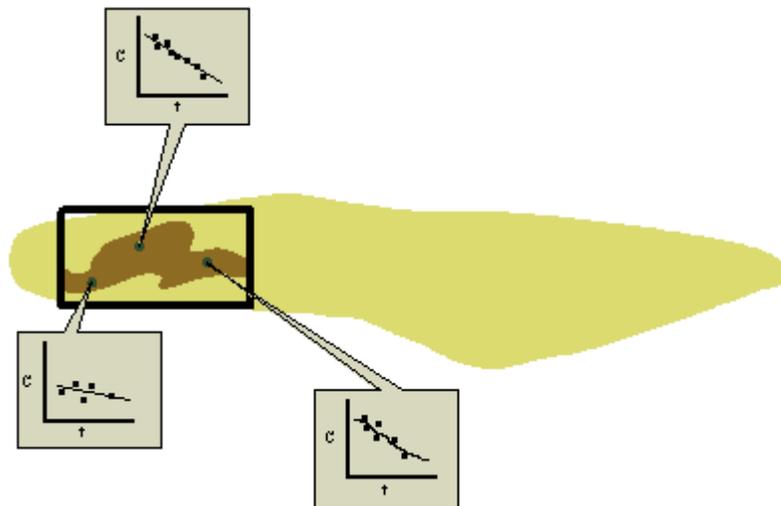
FIGURE 1. SourceDK focus: Change in groundwater concentrations vs. time in the "Source Zone".

SourceDK is intended to be used in four ways:

1. **As a planning tool for developing order-of-magnitude estimates of remediation timeframe.** The SourceDK models and database can be used to help estimate remediation timeframes for natural attenuation and pump-and-treat processes. At most sites, the uncertainty in the estimate will be large. There will likely be smaller uncertainty for sites with these characteristics:

   - fuel hydrocarbon sites;
   - sites with known amount of mass released;
   - sites with extensive groundwater concentration vs. time records;
   - sites with groundwater concentrations that are already close to the remediation objective.

   There will likely be more uncertainty associated with sites that have these characteristics:

- chlorinated solvent sites;
- sites where the mass in the subsurface is unknown;
- sites with limited concentration vs. time records;
- sites with groundwater concentrations that are well above the remediation objective.

Note that there is considerable uncertainty in remediation timeframes for almost all remediation technologies.

2. **As a data management system for storing and interpreting remediation timeframe-related data.** Many sites will continue to be monitored for a long period of time. Data from this monitoring program can be stored in MAROS (Monitoring and Remediation Optimization System, a data management system, http://www.gsi-net.com/software/MAROS.htm) and then used to update remediation timeframe data. This database function can be used in Tier 1, where site data is stored and used to extrapolate remediation timeframes; and in Tier 2, where the data can be used to update and re-calibrate the simple box model.

3. **As a tool for identifying what information is needed to reduce the uncertainty in remediation timeframe estimates.** Applying SourceDK to a site can help users identify what types of data are required to improve the remediation timeframe estimate and reduce the uncertainty in the estimate. Examples of these key data are regular, long-term concentration vs. time records (5 years or more), or more accurate estimates of NAPL and sorbed mass in a source zone.

4. **As a tool for developing source decay rate constants (k_s) that make the source term in other groundwater models more representative of site conditions.** One key concept in SourceDK is that there are different types of first order rate constants that represent very different attenuation processes (see Appendix A.1 for more detail):

   - *Concentration vs. time* rate constants (k_{point}) are used for estimating how quickly remediation goals will be met at a site. In source zones, k_{point} is equivalent to the source decay constant (k_s). **SourceDK can be used to estimate the source decay constant.**

   - *Concentration vs. distance* bulk attenuation rate constants (k) are used for estimating if a plume is expanding, showing relatively little change, or shrinking due to the combined effects of dispersion, biodegradation, and other attenuation processes. **SourceDK does not provide estimates for the bulk attenuation rate constant.**

   - *Biodegradation rate constants* (λ) are used in solute transport models to characterize the effect of biodegradation on constituent migration. **SourceDK does not provide estimates for the biodegradation rate constant.**

In summary, SourceDK can be used to develop the concentration vs. time rate constant (k_{point}), which in source zones is equivalent to the source decay constant (k_s). This source decay constant can then be used in other models, such as BIOCHLOR (Aziz *et al.*, 2000), to account for sources that diminish in strength over time.
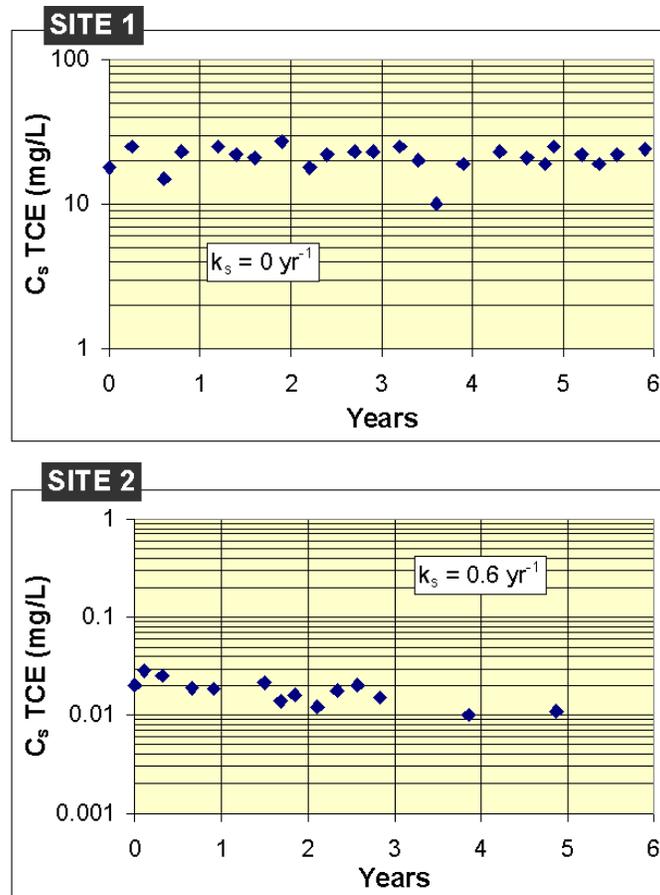
FIGURE 2. Examples of source decay rate constants (k_s) for two monitoring wells at two sites.

SourceDK has the following limitations:

1. **As a planning and screening tool, SourceDK only approximates more complicated processes that occur in the field.** In Tier 1, SourceDK assumes that the estimated trend is maintained throughout the predicted lifetime of the source. In Tier 2, SourceDK assumes the source is represented as a box model and, therefore, simplifies actual site conditions by assuming constant source, hydrogeological, and biological property values for the entire model area. In the Tier 3 NAPL dissolution model, SourceDK assumes uniform flow throughout the source zone, a homogenous aquifer, no biodegradation, and negligible dispersion.

2. **SourceDK simplifies source conditions and does not address some source processes. SourceDK does not address the following processes directly:**

   • Dual Equilibrium Desorption (also referred to as availability or bioavailability effects). Currently there is considerable research dedicated to investigating why organic constituents desorb differently at lower concentrations as compared to higher concentrations. SourceDK does not address this effect directly, and assumes that concentration vs. time trends are maintained throughout the lifetime of the source. For more information on this process, see Luthy *et al.*, 1997 and Chen *et al.*, 2002.

- Vadose-zone sources in Tier 2 or Tier 3 models. SourceDK only assumes a saturated zone NAPL-based source function in the Tier 2 and Tier 3 models. At many sites, this may not affect the remediation timeframe; estimates at most sites are significantly dominated by saturated-zone NAPL sources (Wiedemeier *et al.*, 1999). In other words, the vadose zone sources are much less important than the NAPL sources in the saturated zone. Tier 1 accounts for the impact of vadose zone sources in the extrapolation of groundwater concentration vs. time trends.

- Source zones where matrix diffusion dominates (e.g., see Parker *et al*, 1996).

SourceDK does not address remediation timeframes or the uncertainties associated with intensive source remediation technologies.

SourceDK does not address intensive source zone remediation technologies such as thermal treatment, surfactant/cosolvent flushing, chemical oxidation, or in-situ biodegradation. (Several on-going projects, such as projects funded by the Department of Defense Strategic Environmental Research and Development Program (SERDP) are addressing this issue.)

However, the Tier 1 - Extrapolation tool can be used for any remediation technology as long as it generates some type of concentration vs. time trend data, and all the Tiers in SourceDK can be used to evaluate the time required for the polishing stage to achieve final cleanup after an intensive source zone remediation technology has been applied.

SourceDK MODEL TYPES

The SourceDK Remediation Timeframe software has three different tiers for evaluating reme-diation timeframes:

Tier 1: Empirical Data Trend Extrapolation Model

This model predicts remediation timeframe by determining the trend in measured concentration vs. time data from source-zone monitoring wells (or wells in other parts of the plume) and then extrapolating this trend to determine how long it will take to reach a cleanup objective entered by the user. The trend is based on an analysis of log-concentration vs. time data for any constituent in groundwater.

Figure 3 presents an example of the Tier 1 Empirical Data model. Guidelines for selecting key input parameters for the model are outlined in Tier1 Data Entry. For help on results see Analyzing Tier1 Output.
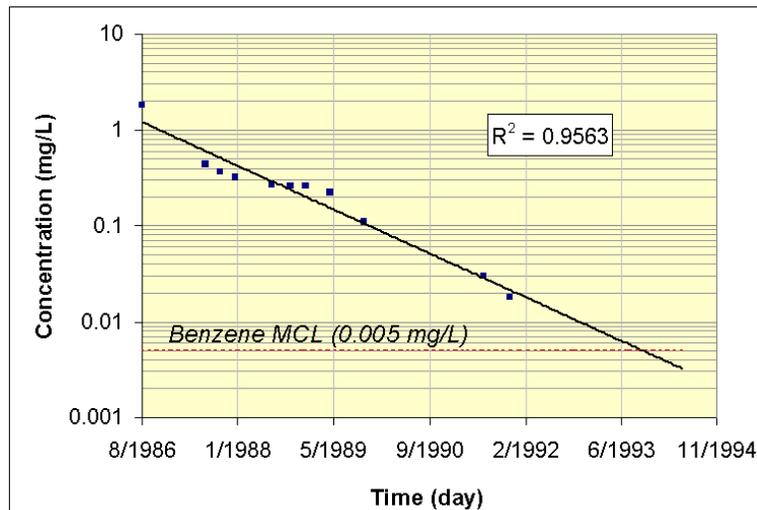
FIGURE 3. Example of empirical data trend extrapolation model. If the trend is extrapolated, the MCL (maximum contaminant level) for benzene will be reached around year 7.

Tier 2: Box Model

This tier predicts concentration vs. time trends assuming the source is a simple box containing constituent mass, there is a certain mass discharge out of the box, and the source concentration vs. time trend will follow a first-order decay pattern. Eqn. 1 is used to estimate the source decay rate constant in the box, which is then used in Eqn. 2 to predict concentration vs. time values. See Figure 4 for an example and Appendix A.2.1 for more detail.

$$k_s = \frac{Q\ C_{gwo}}{M_o}$$

Eqn. 1

$$C_t = C_{gwo} \exp(-k_s t)$$

Eqn. 2

where:

C_t = concentration of dissolved constituent in groundwater at time t (mass/volume)
C_{gwo} = concentration of dissolved constituent in groundwater at time 0 (mass/volume)
Q = specific discharge through the box (volume/time)
M_o = mass in the box at time = 0 (mass)
k_s = source decay rate constant (per time)
t = time (time)
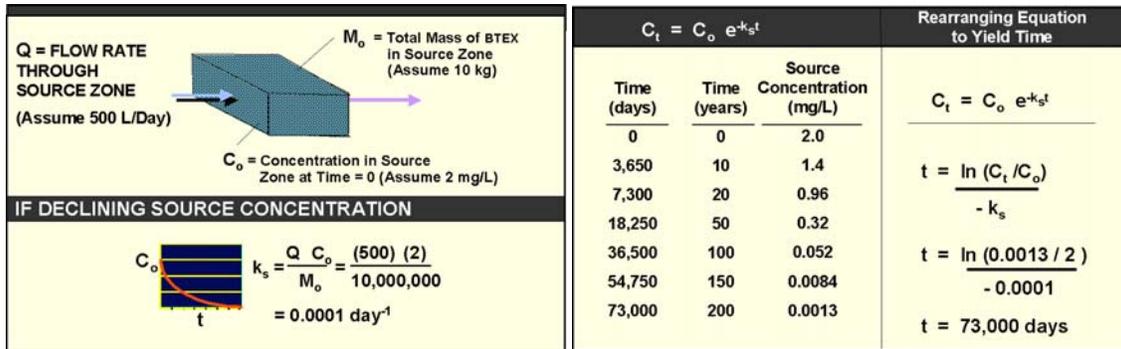
FIGURE 4. Example of source lifetime calculation: declining source concentration.

To account for biodegradation of dissolved-phase constituents in the box (a large sink at many sites), Eqn. 2 and 3 are combined together with biodegradation terms. The complete box model with dissolved-phase biodegradation represented with a biodegradation rate constant (λ can be used for any type of site using Eqn. 3. An alternative model based on biodegradation capacity (Newell *et al.*, 1996) is shown in Eqn. 4, where biodegradation is simulated by entering the concentration of electron acceptors driving the biodegradation (see Appendix A.2.2 for more detail).

$$C_t = C_{gwo} \exp\left\{-\left(\frac{Q_o + \lambda \phi V}{M_o}\right) C_{gwo} t\right\}$$ Eqn. 3

where:

C_t = concentration of dissolved constituent in groundwater at time t (mass/volume)
C_{gwo} = concentration of dissolved constituent in groundwater at time 0 (mass/volume)
Q_o = flowrate of groundwater flowing through the box model (volume/time)
M_o = dissolvable mass of constituent in the source zone box model (typically the total amount of dissolvable material in the NAPL and sorbed to the aquifer material in the saturated zone) (mass)
λ = biodegradation rate constant for the constituent of concern (this is not the same as k_s; see Appendix A.1) (per time)
Φ = porosity (unitless)
V = volume of the box; length times width times thickness (length^3)
t = time (time)

For petroleum hydrocarbon sites, the concentration at any time t ≥ 0 in SourceDK is:

$$C_t = C_{gwo} \exp\left(-\frac{Q_o(C_{gwo} + BC \times \frac{PercentBC}{100})}{M_o} t\right)$$

Eqn. 4

where:

C_t = concentration of dissolved constituent in groundwater at time t (mass/volume)
C_{gwo} = concentration of dissolved constituent in groundwater at time 0 (mass/volume)
Q_o = flowrate of groundwater flowing through the box model (volume/time)
M_o = dissolvable mass of constituent in the source zone box model (typically the total amount of dissolvable material in the NAPL and sorbed to the aquifer material in the saturated zone) (mass)
BC = biodegradation capacity (see Appendix A.3)
PercentBC = percent of biodegradation capacity that is utilized during the biodegradation of the constituent of concern (%)
t = time (time)

Guidelines for selecting key input parameters for the model are outlined in Tier 2 Data Entry. For help on results see Analyzing Tier 2 Output.

Tier 3: Process Models

This tier provides estimates of the time and amount of naturally flowing groundwater required to flush the constituent from the source zone. For zones without any NAPL or matrix diffusion, a Simple Flushing Model, based on one-dimensional advection-dispersion, is used to predict the change in dissolved phase constituent concentrations over time. An approximation of the solution, shown in Figure 5 and Eqn. 5, provides an estimate for the number of pore volumes required to achieve a certain reduction in concentration (see Appendix A.4.1 for more detail). The time required for the groundwater flow to deliver the necessary pore volumes is shown in Eqn. 6. (Note that many fuel hydrocarbon and chlorinated solvent sites are probably impacted by NAPL and matrix diffusion in the source zone, and therefore the use of the simple Flushing Model is likely to be restricted to low concentration organic plumes in clay-free water-bearing units, areas of the plume downgradient of the source zone, or for non-NAPL plumes such as chloride.)

FIGURE 5. Pore volumes required to flush dissolved-phase constituents from porous media assuming no retardation (R=1). To account for retardation, multiply pore volumes by the calculated retardation factor (from Newell *et al.*, 1994).

$$PV = -0.93 \log_{10} \frac{C_t}{C_o} + 0.75$$
Eqn. 5

$$t = \frac{PV \times L}{v_x}$$
Eqn. 6

where:

PV   = pore volumes required to achieve concentration reduction (unitless)
C_t = concentration of dissolved constituent in groundwater at time t (mass/volume)
C_o = original concentration at time t = 0 at any point within the control volume (mass/volume)
t   = time (time)
L   = length along flow path in control volume parallel to groundwater flow (length)
v_x = groundwater seepage velocity (length/time)

NAPL source zones can be evaluated in SourceDK by a simplified version of a single component dissolution model developed by Powers *et al.*, 1994. This simplified model is shown in Figure 6 and described in more detail in Appendix A.4.2.
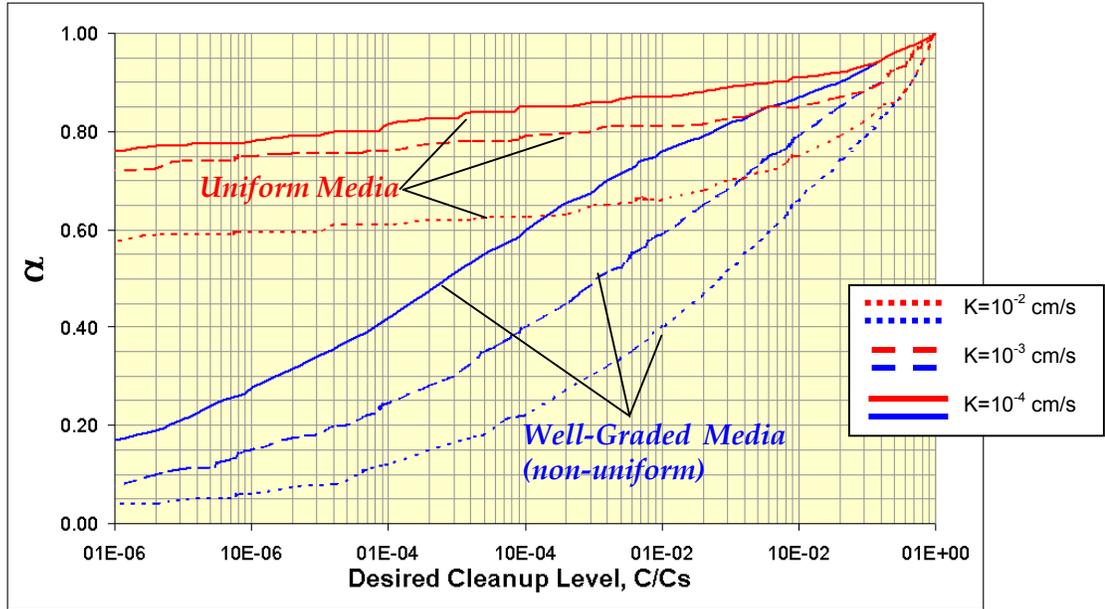
FIGURE 6. Pore volumes required to flush aqueous-phase components from single-component residual NAPL in homogeneous soils (from Newell *et al.*, 1994). α is a solubility scaling coefficient to account for decreasing NAPL solubility as water is flushed through the aquifer (Newell *et al.*, 1994, Powers *et al.*, 1994) and depends on porous media properties. Curves are based on simplification of the theta model developed by Powers *et al.* (1994).

Guidelines for selecting key parameters for this model are outlined in Tier 3 Data Entry. For help on results, see Analyzing Tier 3 Output.

TIER 1 EMPIRICAL DATA TREND EXTRAPOLATION MODEL

[ENTER CONSTITUENT NAME AND HISTORICAL DATA](#)
[WHICH CONSTITUENT TO PLOT?](#)
[OUTPUT GRAPH](#)
[RESULTS](#)

Three important considerations regarding data input are:

1) To see the example data set in the input screen of the software, click on the *Paste Example Data Set* button on the lower right portion of the input screen.
2) Because SourceDK is based on the Excel spreadsheet, you have to click outside of the cell where you just entered data or hit *Return* before any of the buttons will work.
3) Parameters used in the model are to be entered directly into the white cells.

NOTE: The correlation coefficient, r^2, provides a measure of the correlation between concentration and time.

Tier 1 Data Entry: *Enter Constituent Name and Historical Data*

PARAMETER	DATE
Units	Day (m/d/yyyy)
Description	Date when concentration measurements were obtained.
Source of Data	Monitoring wells located near the centerline of the plume.
How to Enter Data	Enter directly. Use arrow keys or the side scroll bar to scroll up and down for additional data entry points. Up to 250 data points can be entered. The "Paste Values" option in Excel can also be used to copy and paste data from an existing table into SourceDK. Do NOT paste "Formats". Do NOT use any "<" signs. All values MUST be greater than or equal to 0.

PARAMETER	CONCENTRATION
Units	mg/L or ug/L
Description	Concentration measurements of dissolved organics in wells near the centerline of the plume obtained after time t = 0. Up to 4 constituents can be entered and viewed individually.
Typical Values	0.0001 - 500 mg/L
Source of Data	Monitoring wells located near the centerline of the plume.
How to Enter Data	1) Enter name of constituent directly below Constituent A, Constituent B, Constituent C, or Constituent D. 2) Select units and enter concentration values directly. Use arrow keys or the side scroll bar to scroll up and down for additional data entry points. Up to 250 data points can be entered. The "Paste" option in Excel can also be used to copy and paste data from an existing table into SourceDK. Do **NOT** use any "<" signs. All values **MUST** be greater than or equal to 0. To "Paste", run Excel again to open a new window. The table to paste values from MUST be in this new Excel window. Copy the columns to paste into SourceDK, switch to the SourceDK window and select "Paste" option in Excel to paste the data into SourceDK. Please note that any data not recognized as a positive number will not be used in the analysis.

PARAMETER:	PRINT HISTORICAL DATA
Description	Prints historical data on the default printer. To print on a different printer, select the printer in the "Print" options in Excel and then press the "Print Historical Data" button.

Tier 1 Data Entry: *Which Constituent to Plot?*

PARAMETER:	CONSTITUENT TO PLOT
Description	Choice of constituent to be plotted.
How to Enter Data	1) Enter Clean-Up Level for constituent of choice 2) Select the constituent to be plotted..

PARAMETER	WHAT IS THE CLEAN-UP LEVEL?
Units	mg/L or ug/L
Description	Desired clean-up level to be achieved by the constituent of choice.
Source of Data	Regulatory agencies, such as MCLs or Protective Concentration Levels, or values derived from risk assessments.
How to Enter Data	Enter directly.

Tier 1 Data Entry: *Output Graph*

PARAMETER:	GRAPH OUTPUT
Description	Concentration versus time data is plotted on a semi-logarithmic scale. The model calculates the date when the desired clean-up level (entered in Section 2) for the chosen constituent will be reached.
How to Enter Data	1) Enter Clean-Up Level for constituent of choice 2) Select the constituent to be plotted. **Please note that if the units are changed after the constituent has been selected and the graph created then the "Update Graph" button must be pressed for the graph to be re-created in the selected units.** The format of the graph can temporarily be changed by selecting "Tools", then "Protection", then "Unprotect Sheet" from the Excel Toolbar. Double clicking on the graph will allow editing. **Please note that if any of the Toolkit functions are used ("Update Graph", Selection of a COC, etc) the graph will revert back to the original version. However, exiting the Tier and returning does not affect the graph formatting.**

PARAMETER:	NUMBER OF YEARS OVER WHICH TO PLOT GRAPH
Units	yr
Description	Time period over which to view graph.
Typical Values	1 - 1000 years
Source of Data	To match an existing plume, estimate the time between the original release and the date the field data were collected. Default value used is the period over which the field data is available.
How to Enter Data	Enter directly. 1) Enter the Number of Years Over Which to Plot Graph. 2) Click on the *Update Graph* button to update graph.

Analyzing Tier 1 Output

PARAMETER:	PREDICTED DATE TO ACHIEVE CLEANUP
Description	The model uses exponential extrapolation to calculate the most probable date and the 90% or 95% prediction levels when the desired clean-up level (entered in Section 2) for the chosen constituent will be reached. All analyses are based on the earliest sampling event date entered in Section 1. (See Appendix A.5 for more detail on the 95% confidence limit calculation). The model presents values for the most predicted date to achieve cleanup and the lower and upper confidence limits of the chosen confidence interval. The following rules apply to the prediction of cleanup dates: 1) The model calculates dates for decreasing concentration trends only. For increasing concentration trends (plumes with positive slopes), the model will show the message "Can't Calc (+ve trend)". 2) For cleanup levels greater than the

	concentration of the *earliest* point of the predicted trend, the predicted cleanup date is the year of the *earliest* sample entered in the Constituent Historical Data section.
How to Enter Data	Select the 90% or 95% option button.

PARAMETER:	SOURCE DECAY RATE CONSTANT (k_s)
Description	The model uses a first-order decay relationship to describe how quickly the dissolved concentrations in the source zone (i.e., concentrations that are directly controlled by the rate of NAPL dissolution and/or the rate of desorption from the aquifer material) decline over time. This rate constant is not the same rate constant that represents the attenuation of dissolved-phase constituents that have left the source zone or the biodegradation of dissolved constituents. (See Appendix A.1 of the SourceDK User's Manual for more information.) Decreasing concentration trends are represented with a positive Source Decay Rate Constant (k_s), while increasing concentrations with a negative k_s.

TIER 2: BOX MODEL

The Main Screen offers two options for proceeding to the Tier 2 data input screen:

1) The *Enter New Site* option clears out any previously entered site information in the Tier 2 input screen.
2) The *View Last Entered Site* option maintains all the information that was last entered in Tier 2.

HYDROGEOLOGY
SOURCE CHARACTERISTICS
SOURCE DECAY CONSTANT
SOURCE MASS
SOURCE ZONE BIODEGRADATION
TIME FOR OUTPUT
UNCERTAINTY RANGE
FIELD DATA FOR COMPARISON
ANALYZING TIER 2 OUTPUT

Three important considerations regarding data input are:

1) To see the example data set in the input screen of the software, click on the *Paste Example Data Set* button on the lower right portion of the input screen.
2) Because SourceDK is based on the Excel spreadsheet, you have to click outside of the cell where you just entered data or hit *Return* before any of the buttons will work.
3) Parameters used in the model can be entered directly into the white cells or they can be calculated by the model using data entered in the grey cells (e.g., Darcy velocity can be entered directly or calculated using hydraulic conductivity and hydraulic gradient followed by pressing the *Calculate Vd* button).

NOTE: Although literature values are provided, it is strongly recommended that the user employ measured hydrogeological and source characteristic values whenever possible. If literature values are used and there is uncertainty in the value chosen, sensitivity analyses should be conducted to determine the effects of the uncertainty on model predictions.

Tier 2 Data Entry: *Hydrogeology*

PARAMETER:	DARCY VELOCITY (V$_d$)
Units	ft/yr
Description	Groundwater Darcy velocity through the *Box* (the source zone). Note that SourceDK is not formulated to simulate the effects of chemical diffusion. Therefore, contaminant transport through very slow hydrogeologic regimes (e.g., clays and slurry walls) should probably not be modeled using SourceDK unless the effects of chemical diffusion are proven to be insignificant.
Typical Values	0.2 - 200 ft/yr (Newell *et al.*, 1990)
Source of Data	Calculated by multiplying hydraulic conductivity by hydraulic gradient (V$_d$ = K * i). Use of actual site data for hydraulic conductivity and hydraulic gradient parameters is strongly recommended.
How to Enter Data	1) Enter directly, or 2) Fill in values for hydraulic conductivity and hydraulic gradient and have SourceDK calculate Darcy velocity by pressing the *Calculate Vd* button.

PARAMETER:	HYDRAULIC CONDUCTIVITY (K)
Units	cm/sec, ft/d, or ft/yr
Description	Measure of the permeability of the saturated porous medium.
Typical Values	Clays: $<1\times10^{-6}$ cm/s Silts: 1×10^{-6} - 1×10^{-3} cm/s Silty sands: 1×10^{-5} - 1×10^{-1} cm/s Clean sands: 1×10^{-3} - 1 cm/s Gravels: > 1 cm/s (Newell *et al.*, 1996)
Source of Data	Pump tests or slug tests at the site. It is strongly recommended that actual site data be used for all RNA studies.
How to Enter Data	Enter directly and choose appropriate units for the values entered. This parameter is not needed in SourceDK if Darcy velocity is entered directly.

PARAMETER:	HYDRAULIC GRADIENT (i)
Units	ft/ft
Description	The slope of the potentiometric surface. In unconfined aquifers, this is equivalent to the slope of the water table.
Typical Values	0.001- 0.1 ft/ft
Source of Data	Calculated by constructing potentiometric surface maps using static water level data from monitoring wells and estimating the slope of the potentiometric surface.
How to Enter Data	Enter directly. This parameter is not needed in SourceDK if Darcy velocity is entered directly.

Tier 2 Data Entry: *Source Characteristics*

PARAMETER	SOURCE GROUNDWATER CONCENTRATION (C_{gwo})
Units	mg/L
Description	**Aqueous** phase concentration of constituents in the source zone at time t = 0.
Typical Values	0.0001 - 500 mg/L
Source of Data	Source area monitoring well data at the time simulation is to start.
How to Enter Data	Enter directly.

PARAMETER:	SOURCE LENGTH (S_l)
Units	ft
Description	Estimated length of the box model of the source zone parallel to groundwater flow.
Typical Values	10-500 ft
Source of Data	To determine source length across the site, draw a line parallel to the direction of groundwater flow in the source area. The source area is the zone where mass is entering groundwater, due to leaching from the vadose zone, dissolution of NAPLs, desorption of aquifer materials, and/or matrix diffusion.
How to Enter Data	Enter directly.
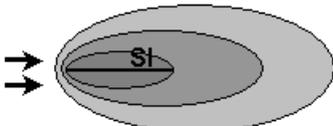
PARAMETER:	SOURCE WIDTH (S_w)
Units	ft
Description	The estimated width of the box model of the source zone perpendicular to the groundwater flow.
Typical Values	0-500 ft
Source of Data	To determine source width across the site, draw a line perpendicular to the direction of groundwater flow in the source area. The source area is the zone where mass is entering groundwater, due to leaching from the vadose zone, dissolution of NAPLs, desorption of aquifer materials, and/or matrix diffusion. If the source zone covers a large area, it is best to choose the most downgradient or widest point in the source area for determining the source width.
How to Enter Data	Enter directly.
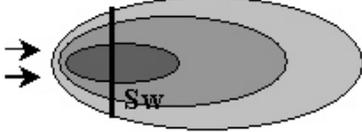
PARAMETER	SOURCE THICKNESS (S_t)
Units	ft
Description	The estimated saturated thickness of the box model of the source zone.
Typical Values	5 - 50 ft
Source of Data	This parameter is typically determined from site boring logs or estimated as maximum known thickness plus some fixed distance (e.g. 10 ft). For LNAPL sites, a value of 6 ft is used for many modeling studies. As with source length and source width, the source zone thickness is the zone where mass is entering groundwater, due to leaching from the vadose zone, dissolution of NAPLs, desorption of aquifer materials, and/or matrix diffusion.
How to Enter Data	Enter directly.
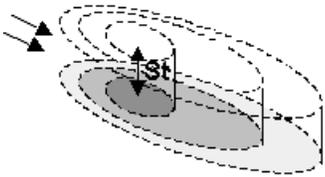
PARAMETER:	SPECIFIC DISCHARGE (Q)
Units	ft^3/yr
Description	Groundwater flow through source zone
Typical Values	$100 - 10^6$ ft^3/yr
Source of Data	Calculated from dimensions of the box and Darcy velocity for groundwater.
How to Enter Data	1) Enter directly, or 2) Have SourceDK calculate Specific Discharge by pressing the *Calculate Q* button.

Tier 2 Data Entry: *Source Decay Constant*

The user may select to enter the Source Decay Constant directly or calculate it using source mass and biodegradation information.

PARAMETER:	SOURCE DECAY CONSTANT (k_s)
Units	yr^{-1}
Description	The Source Decay Rate Constant is used in a first-order decay relationship to describe how quickly the dissolved concentrations in the source zone (i.e., concentrations that are directly controlled by the rate of NAPL dissolution and/or the rate of desorption/diffusion from the aquifer material) decline over time. This rate constant is not the same rate constant that represents the attenuation of dissolved-phase constituents that have left the source zone (k) or the biodegradation of dissolved constituents (λ) (see Appendix A.1 for more detail).
Representative Values	Benzene – 0.16 - 0.30 yr^{-1} PCE – 0.03 - 0.50 yr^{-1} Toluene – 0.38 - 0.44 yr^{-1} TCE – 0.04 - 0.18 yr^{-1} Ethylbenzene – 0.16 - 0.22 yr^{-1} cis-DCE – 0.11 - 0.81 yr^{-1} Xylenes – 0.19 - 0.25 yr^{-1} TCA – 0.04 - 0.31 yr^{-1} MTBE – 0.15 - 0.31 yr^{-1} 1,2-DCA – 0.02 - 0.30 yr^{-1} (Mace, 1997; McNab *et al.*, 1999; and McNab, 2001)
Source of Data	SourceDK source decay constant database derived from an analysis of data in two databases: 1) petroleum hydrocarbon underground storage tank sites in Texas developed by Mace (1997) and 2) chlorinated solvent sites database developed by McNab *et al*. (1999) and McNab (2001). See "Background Information for SourceDK Modeling" section below for more detail.
How to Enter Data	1) Enter directly, or 2) Calculate using site data.

Tier 2 Data Entry: *Source Mass*

The user may select one of four methods for calculating source mass by selecting the appropriate button. This choice will determine which of the calculation methods is used, as well as controlling the appearance of the screen, and determining which data entry cells are unlocked.

Method 1: Enter Source Mass Directly
Method 2: Simple Volume x Concentration Calculation
Method 3: Detailed Volume x Concentration Calculation
Method 4: Estimated From NAPL Relationships

Tier 2 Source Mass Method 1:
Enter Source Mass Directly

PARAMETER	SOURCE MASS
Units	kg
Description	The amount of the constituent of interest that is contained in different "compartments" in the source zone: 1) the free-phase or residual NAPLs compartment; 2) the compartment representing the constituent mass that is sorbed to aquifer material; and 3) the dissolved mass in groundwater in the source zone (this last term is small relative to the other two terms and can be ignored at many sites). The total "source mass" of a constituent is used to estimate the rate at which the source zone concentration of this constituent declines. Note that the following two compartments are <u>not</u> directly considered in the SourceDK Tier 2 Box Model: 1) vadose zone sources leaching into the saturated zone; and 2) sources caused by matrix diffusion in low permeability zones. SourceDK has a calculation module to help estimate this value.
Typical Values	0.10 – 100,000 kg
Source of Data	See SourceDK calculation module.
How to Enter Data	Enter directly or use SourceDK to calculate mass.

Tier 2 Source Mass Method 2:
Simple Volume x Concentration Calculation

PARAMETER	AVERAGE CONSTITUENT CONCENTRATION IN SATURATED SOURCE ZONE
Units	mg/kg
Description	Average of the soil phase concentration of the constituent in the source zone at time t=0.
Typical Values	0.010 - 1000 mg/kg
Source of Data	Source area saturated zone soil samples.
How to Enter Data	Enter directly.

PARAMETER	SOIL BULK DENSITY
Units	kg/L or g/cc
Description	Density of the dry aquifer material (referred to as "soil").
Typical Values	Although this value can be measured in the lab, in most cases estimated values are used. A value of 1.7 kg/L is used frequently.
Source of Data	Either from an analysis of soil samples at a geotechnical lab or more commonly, application of estimated values such as 1.7 kg/L.

How to Enter Data	Enter directly.

Tier 2 Source Mass Method 3:
Detailed Volume x Concentration Calculation

When **Method 3** of calculation is chosen, actual groundwater data and saturated soil constituent concentration data are used to calculate source mass. The user may define three mass "compartments": 1) saturated zone NAPL, 2) dissolved mass in the saturated zone, and 3) sorbed mass (storage in a "matrix diffusion compartment" is not directly considered). For each compartment the user enters actual concentration measurements in soil or groundwater (up to 30 data points), as well as specifies which of four averaging methods will be used: arithmetic mean, geometric mean, area-weighted average (user-specified areas), or area-weighted average (user-specified data points). Data for each compartment can be edited by clicking on the *Enter Data* button.

For the arithmetic mean, geometric mean, and area-weighted average (user-specified areas) methods, the user enters soil/groundwater concentrations and layer dimensions, and the model computes the mass for that layer.

When the area-weighted average (user-specified data points) method is chosen, the user must specify shape of the layer, concentration measurements, and locations of the data points. To update the compartment mass calculation using this method, the user must click on the *Calculate Layer Mass* button after each change in the data. The model assigns concentration values to each cell based on the closest user-input data point.

Tier 2 Source Mass Method 3:
Enter Site Data

PARAMETER	SATURATED ZONE TOTAL POROSITY
Units	Unitless
Description	Dimensionless ratio of the volume of voids to the bulk volume of the surface soil column matrix. Note that *total porosity* is the ratio of all voids (including non-connected voids) to the bulk volume of the aquifer matrix. Differences between total and effective porosity reflect lithologic controls on pore structure. In unconsolidated sediments coarser than silt size, effective porosity can be less than total porosity by 2-5% (e.g. 0.28 vs. 0.30) (Smith and Wheatcraft, 1993).
Typical Values	Values for Effective Porosity: Clay 0.01 - 0.20 Sandstone 0.005 - 0.10 Silt 0.01 - 0.30 Gravel 0.10 - 0.35 Fract. Granite 0.00005 - 0.01 Unfract. Limestone 0.001- 0.05 Fine Sand 0.10 - 0.30 Medium Sand 0.15 - 0.30 Coarse Sand 0.20 - 0.35 (From Wiedemeier *et al.*, 1999; originally from Domenico and Schwartz, 1990 and Walton, 1988).
Source of Data	Typically estimated. One commonly used value for silts and sands is an effective porosity of 0.25. The ASTM RBCA Standard (ASTM, 1995) includes a default value of 0.38 (to be used primarily for unconsolidated deposits).
How to Enter Data	Enter directly.

PARAMETER	SATURATED ZONE SOIL DENSITY
Units	g/cm^3
Description	Density of the saturated aquifer material (referred to as "soil"), including soil moisture.
Typical Values	Although this value can be measured in the lab, in most cases estimated values are used. A value of 2.0 - 2.2 g/cm^3 is used frequently. Note that the soil density in the water-bearing unit should generally be larger than in the surface soil zone due to its higher water content.
Source of Data	Typically estimated or derived from an analysis of soil samples at a geotechnical lab.
How to Enter Data	Enter directly.

PARAMETER	RETARDATION FACTOR
Units	Unitless
Description	The retardation factor is the ratio of the dissolved plus sorbed constituent mass to the dissolved constituent mass in the aqueous phase in a unit volume of aquifer. The retardation factor is a function of both aquifer and constituent properties.

Typical Values	1-3 (typical for BTEX)
	2-5 (typical for chlorinated solvents)
Source of Data	Usually estimated from soil and chemical data using the following expression:
	$R = 1 + K_d \cdot \rho_d / n$
	where $K_d = K_{oc} \cdot f_{oc}$
	where ρ_d = bulk density, n = porosity, K_{oc} = organic carbon-water partition coefficient, K_d = distribution coefficient, and f_{oc} = fraction organic carbon on uncontaminated soil.
How to Enter Data	Enter directly.

Tier 2 Source Mass Method 3:
Enter Zone Data

Data input procedure:

1) Press *Enter Data* button then select the data averaging method.
2) Press *Edit Layer for This Layer*.
3) Enter layer dimensions and concentration data for that layer.
4) Press *Return*.
5) Repeat steps 1 though 4 for next zone.

Tier 2 Source Mass Method 3:
Constituent Mass Located in the Saturated Zone NAPL

Constituents contained as NAPL make up the first compartment, which can be the most important compartment for estimating source mass at many sites.

1) First, the horizontal extent of the NAPL zone is established by mapping the area with wells containing NAPLs or by estimating the presence of NAPLs based on concentrations of dissolved hydrocarbon constituents greater than some threshold value (e.g., >1% solubility). For gasoline sites, values > 3000 ppb total BTEX have been proposed by Gallagher *et al.* (1995) as being representative of the NAPL zone. The 1% rule (Newell and Ross, 1992) has been used to estimate the presence of NAPL.

2) Second, soil samples located inside the source area both laterally and vertically are then averaged using one of the techniques described below to determine the average soil concentration in the NAPL zone.

3) Multiply i) the average concentration by ii) the volume inside the assumed NAPL zone and by iii) the assumed soil density to calculate source mass.

Tier 2 Source Mass Method 3:
Constituent Mass Located in the Dissolved Compartment

The second compartment to be considered is the saturated zone (dissolved phase) groundwater located in the source zone. This compartment will typically contain only a small fraction of the mass contained in the other compartments.

1) The source area for dissolved groundwater can be assumed to be of the same lateral extent as the Saturated NAPL zone, if the NAPL zone exists at the site. If no NAPL zone is known to exist at the site, then the groundwater source area should be defined as the area inside some contour of known concentration (i.e., 1000 ppb total BTEX).

2) Groundwater concentrations located inside the source area are then averaged both spatially and temporally using one of the techniques described below.

3) Multiply the average concentration by i) the area of affected groundwater, ii) by the assumed or actual vertical extent and by iii) the porosity to determine dissolved mass of constituents of concern.

Tier 2 Source Mass Method 3:
Sorbed Constituent Compartment

The third compartment to be considered is the sorbed constituent located in the source zone. This compartment represents the sorption of dissolved constituents onto the solid aquifer matrix that results in the slowing of the dissolved constituents moving through an aquifer. This mass is calculated automatically by SourceDK and is the product of the dissolved constituent mass and the retardation factor -1.

Tier 2 Source Mass Method 3:
Spatial Averaging Techniques

Use of Method 3 of source mass calculation requires that data points within each compartment be averaged together to get a concentration representative of the entire layer. SourceDK includes several methods for calculating samples as described below:

Arithmetic Mean: The simplest averaging technique is the arithmetic mean. The user may average all data located within the compartment or depth interval, or may alternately censor closely spaced samples to create a more representative statistical sample. The mass calculated with this method is very sensitive to the total source area, and is often the least accurate of the methods provided. The equation for the arithmetic mean for *n* data points is:

$$\overline{C} = \frac{C_1 + C_2 + \cdots + C_n}{n}$$

Eqn. 7

Geometric Mean: Another option for averaging multiple data points within a compartment or depth interval is the geometric mean. The geometric mean is useful for a dataset which is logarithmically distributed or whose members vary over orders of magnitude. It is often used in the analysis of environmental data to account for lognormal data distributions. The equation for the geometric mean for *n* data points is:

$$\overline{C} = \sqrt[n]{C_1 \times C_2 \times \cdots \times C_n}$$

Eqn. 8

Area-Weighted Average: A third averaging technique is area-weighted averaging. This technique addresses a major weakness of the other techniques discussed above because each data set is given a weight based on the area it represents. No data censoring is necessary because closely spaced data do not bias the results. SourceDK allows the user to specify the area, *A*, which applies to each sample, or it will approximate the area if the user has not already done so.   The equation for the area-weighted average for *n* data points, each being representative of an area, *A*, is:

$$\overline{C} = \frac{C_1 \times A_1 + C_2 \times A_2 + \cdots + C_n \times A_n}{A_1 + A_2 + \cdots + A_n}$$

Eqn. 9
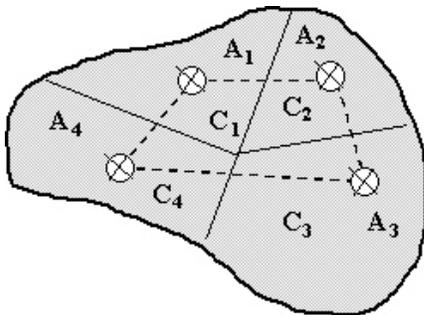
Tier 2 Source Mass Method 3: *Layer Shape and Dimension Calculation*

PARAMETER	LAYER THICKNESS
Units	ft
Description	Thickness of the affected layer for the compartment and the layer of interest.
Typical Values	5 - 50 ft
Source of Data	Based on vertical discretization of compartment of interest from saturated soil samples or vertical distribution of affected groundwater.
How to Enter Data	Enter directly.

PARAMETER	AFFECTED AREA
Units	ft^2
Description	Area of the affected layer for the compartment of interest for the arithmetic and geometric mean averaging methods.
Typical Values	100 – 500,000 ft^2
Source of Data	Map of estimated extent of the compartment of interest (either the saturated NAPL compartment or the dissolved compartment).
How to Enter Data	Enter directly.

PARAMETER	SOIL CONCENTRATION (FOR SATURATED ZONE NAPL ONLY)
Units	mg/kg
Description	Multiple **soil** phase concentration of constituents in the saturated NAPL source zone compartment at time t=0 for the layer of interest.
Typical Values	0.010 - 1000 mg/kg
Source of Data	Source area saturated zone soil samples.
How to Enter Data	Enter directly.

PARAMETER	GROUNDWATER CONCENTRATION (FOR DISSOLVED COMPARTMENT ONLY)
Units	mg/L
Description	**Dissolved** concentration of constituents in dissolved compartment at time t=0 for the layer of interest.
Typical Values	0.010 - 1000 mg/L
Source of Data	Source area monitoring well data.
How to Enter Data	Enter directly.

Tier 2 Source Mass Method 3:
User Input Area-Weighted Average Layer Shape and Dimension Calculation

When the area-weighted average (user-specified data points) method is chosen, the user must specify concentration measurements as well as locations of the data points.

PARAMETER	LAYER THICKNESS
Units	ft
Description	Thickness of the affected layer for the compartment of interest.
Typical Values	5 - 50 ft
Source of Data	Map of estimated extent of the compartment being evaluated (either the saturated NAPL compartment or the dissolved compartment).
How to Enter Data	Enter directly.

PARAMETER	LAYER LENGTH
Units	ft
Description	Length of the affected layer for the compartment of interest.
Typical Values	10 - 2000 ft
Source of Data	Map of estimated extent of the compartment being evaluated (either the saturated NAPL compartment or the dissolved compartment).
How to Enter Data	Enter directly.

PARAMETER	LAYER WIDTH
Units	ft
Description	Width of the affected layer for the compartment of interest.
Typical Values	10 - 1000 ft
Source of Data	Map of estimated extent of the compartment being evaluated (either the saturated NAPL compartment or the dissolved compartment).
How to Enter Data	Enter directly.

PARAMETER	SOIL CONCENTRATION (FOR THE SATURATED ZONE NAPL ONLY)
Units	mg/kg
Description	Multiple **soil** phase concentration of constituents in the saturated NAPL source zone compartment at time t=0 for the layer of interest.
Typical Values	0.010 - 1000 mg/kg
Source of Data	Source area saturated zone soil samples
How to Enter Data	Enter directly.

PARAMETER	GROUNDWATER CONCENTRATION (FOR THE DISSOLVED COMPARTMENT ONLY)
Units	mg/L
Description	**Dissolved** concentration of constituent in dissolved compartment at time t=0 for the layer of interest.
Typical Values	0.010 - 1000 mg/L
Source of Data	Source area monitoring well data.
How to Enter Data	Enter directly.

PARAMETER	AREA
Units	ft^2
Description	Area of the affected sample for the compartment of interest.
Typical Values	100 – 500,000 ft^2
Source of Data	Map of estimated extent of saturated NAPL source zone compartment, or the dissolved compartment, depending on which compartment data is being entered for.
How to Enter Data	Enter directly.

PARAMETER	LAYER SHAPE
Description	Shape of affected layer.
How to Enter Data	Select either elliptical or rectangular layer shape depending on which shape best represents the affected area of the compartment and layer of interest.

Tier 2 Source Mass Method 4: *Estimated From NAPL Relationships*

PARAMETER	NAPL SATURATION
Units	Unitless
Description	An estimate of the fraction of the pore space filled with NAPL.
Typical Values	0 – 0.30. For a discussion of saturation at solvent sites, see Pankow and Cherry, 1996. For a detailed discussion of solvents and fuels, see Mercer and Cohen, 1990. For a brief summary see Chapter 2 of Wiedemeier *et al.*, 1999.
Source of Data	This value can be measured by analyzing soil samples. Without site specific measurements, the uncertainty in the estimates will likely be an order-of-magnitude or greater.
How to Enter Data	Enter directly.

PARAMETER	CONSTITUENT MASS FRACTION
Units	Percent
Description	Chemical- and mixture-specific value expressing how much of a mixture consists of one particular constituent, on a mass basis, such as how much of a gasoline sample consists of benzene. Constituent mass fraction $\quad f_i = \dfrac{mass_i}{mass_{mixture}}$
Typical Values	Typical ranges for mass fractions in fresh gasoline for BTEX compounds (Kostecki & Calabrese, 1993): Minimum Maximum Benzene 0.12 3.5% Ethylbenzene 0. 36 2.86% Toluene 2.73 21.8% Xylene 3.22 8.31% Note that there is a wide range of reported values for gasoline, depending on grade, manufacturer, and the age of the spill. Mass fraction for solvent sites is very site specific, and no general rules or estimation techniques are available without a chemical analysis of the NAPL.
Source of Data	Chemical reference literature for fuels, or fingerprinting analysis for either solvents or fuels.
How to Enter Data	Enter directly.

PARAMETER	DENSITY OF SOURCE NAPL
Units	g/cm^3
Description	Density of the source NAPL.
Typical Values	0.80 to 1.4.
Source of Data	From an analysis of NAPL samples or from literature values.
How to Enter Data	Enter directly.

PARAMETER	SATURATED ZONE TOTAL POROSITY
Units	Unitless
Description	Dimensionless ratio of the volume of interconnected voids to the bulk volume of the aquifer matrix. Note that *total porosity* is the ratio of all voids (including non-connected voids) to the bulk volume of the aquifer matrix. Differences between total and effective porosity reflect lithologic controls on pore structure. In unconsolidated sediments coarser than silt size, effective porosity can be less than total porosity by 2-5% (e.g. 0.28 vs. 0.30) (Smith and Wheatcraft, 1993).
Typical Values	Values for Effective Porosity: Clay 0.01 - 0.20 Sandstone 0.005 - 0.10 Silt 0.01 - 0.30 Gravel 0.10 - 0.35 Fract. Granite 0.00005 - 0.01 Unfract. Limestone 0.001- 0.05 Fine Sand 0.10 - 0.30 Medium Sand 0.15 - 0.30 Coarse Sand 0.20 - 0.35 (From Wiedemeier *et al.*, 1999; originally from Domenico and Schwartz, 1990 and Walton, 1988).
Source of Data	Typically estimated. One commonly used value for silts and sands is an effective porosity of 0.25. The ASTM RBCA Standard (ASTM, 1995) includes a default value of 0.38 (to be used primarily for unconsolidated deposits).
How to Enter Data	Enter directly.

Tier 2 Data Entry:
Source Zone Biodegradation Data

There are three options available here: 1) no biodegradation, 2) a method to account for source mass that is lost due to biodegradation in the box model by entering a biodegradation rate constant for any dissolved constituent that biodegrades (this is the most common, and simplest method), and 3) a method to account for source mass that is lost due to biodegradation in the box model by entering the biodegradation capacity (this is only for fuel sites and the BTEX constituents, and is more complex). SourceDK assumes that all the biodegradation takes place in the dissolved phase and only acts on dissolved constituent in the box (the control volume). It is important to consider this sink for the constituent being modeled, because it can be significant at many sites.

PARAMETER	NO BIODEGRADATION
Description	Decay without biodegradation.
How to Enter Data	Select radio button for this option.

PARAMETER	BIODEGRADATION RATE CONSTANT (lambda)
Units	1/yr
Description	Rate coefficient describing the biodegradation of dissolved constituents in groundwater. This is different than k_s, the source decay rate constant (see Appendix A.1).
Typical Values	Benzene 0.35 to 35 yr^{-1} Toluene 4.1 to 35 yr^{-1} Ethylbenzene 1.1 to 43 yr^{-1} Xylene 0.69 to 18 yr^{-1} (calculated from half-lives from ASTM, 1995) Perchloroethylene 0.069 to 1.2 yr^{-1} Trichloroethylene 0.051 to 0.91 yr^{-1} cis-1,2- Dichloroethylene 0.18 to 3.3 yr^{-1} Vinyl Chloride 0.12 to 2.6 yr^{-1} (from Wiedemeier *et al.*, 1999.) See Appendix A.1 for more information.
Source of Data	Optional methods for selection of appropriate decay coefficients are as follows: **Literature values**: Various published references are available listing decay half-life values for hydrolysis and biodegradation (e.g., see Howard *et al.*, 1991). Note that many references report the half-lives; these values can be converted to the first-order decay coefficients using $k = 0.693 / t_{1/2}$. **From site studies:** Biodegradation rate constants can be obtained from calibrated groundwater models.

	For more information see Appendix A.1.
How to Enter Data	Enter directly. This cell will be white with black text and data may be entered directly only when *Method 1* is chosen, otherwise this cell will be black and locked.

PARAMETER	BIODEGRADATION CAPACITY (BC)
Units	mg/L
Description	*Note: this parameter is only applicable to studies of fuel hydrocarbon sites with benzene, toluene, xylenes, or ethylbenzene (BTEX) as the constituent (not applicable to MTBE).* Biodegradation capacity (also called expressed assimilative capacity) is an estimate of the amount of biodegradation that upgradient groundwater can support. It is calculated by evaluating the difference between electron acceptors (dissolved oxygen, nitrate, and sulfate) in upgradient vs. source wells, and accounting for the production of metabolic by-products in the source zone (i.e., ferrous iron and methane). These values are then adjusted to normalize the amount of consumed electron acceptors and produced metabolic by-products by the stoichiometry of the biodegradation reaction with BTEX constituents. For more information, see Newell *et al.*, 1996 or Wiedemeier *et al.*, 1999.
Typical Values	7 - 70 mg/L
Source of Data	From site monitoring well data (both clean upgradient wells, and source zone wells).
How to Enter Data	1) Enter directly, or 2) Have SourceDK calculate the value by pressing the *Calculate BC* button. This cell will be white with black text and data may be entered directly only when *Method 2* is chosen, otherwise this cell will be black and locked.

PARAMETER	DELTA OXYGEN (DO)
Units	mg/L
Description	This parameter, used in the biodegradation model, is one component of the total biodegradation capacity of the groundwater as it flows through the source zone and constituent plume. The model assumes that 3.14 mg of oxygen are required to consume 1 mg of BTEX (Wiedemeier *et al.*, 1995).
Typical Values	Data from 28 AFCEE sites: Median = 5.8 mg/L Maximum = 12.7 mg/L Minimum = 0.4 mg/L
Source of Data	Site monitoring well data. When measuring DO in the field, the Air Force Intrinsic Remediation Technical Protocol (Wiedemeier *et al.*, 1995) can be applied. Enter the average background concentration (average upgradient concentration can be used if background information in unavailable) of oxygen minus the lowest observed concentration of oxygen in the source area. The model automatically applies the utilization factor to compute a biodegradation capacity.

How to Enter Data	Enter directly. This cell will be gray with black text and data may be entered directly only when *Method 2* is chosen, otherwise this cell will be black and locked. A value of zero is used if no data is entered.

PARAMETER	DELTA NITRATE (NO₃)
Units	mg/L
Description	This parameter, used in the biodegradation model, is one component of the total biodegradation capacity of the groundwater as it flows through the source zone and constituent plume. The model assumes that 4.9 mg of nitrate are required to consume 1 mg of BTEX (Wiedemeier *et al.*, 1995).
Typical Values	Data from 28 AFCEE sites: Median = 6.3 mg/L Maximum = 69.7 mg/L Minimum = 0 mg/L
Source of Data	Site monitoring well data. When measuring nitrate in the field, the Air Force Intrinsic Remediation Technical Protocol (Wiedemeier *et al.*, 1995) can be applied. Enter the average background concentration (average upgradient concentration can be used if background information in unavailable) of nitrate minus the lowest observed concentration of nitrate in the source area. The model automatically applies the utilization factor to compute a biodegradation capacity.
How to Enter Data	Enter directly. This cell will be gray with black text and data may be entered directly only when *Method 2* is chosen, otherwise this cell will be black and locked. A value of zero is used if no data is entered.

PARAMETER	OBSERVED FERROUS IRON (Fe^{2+})
Units	mg/L
Description	This parameter is one component of the total biodegradation capacity of the groundwater as it flows through the source zone and constituent plume. Ferrous iron is a metabolic by-product of the anaerobic reaction where solid ferric iron is used as an electron acceptor. The model assumes that 21.8 mg of ferrous iron represents the consumption of 1 mg of BTEX (Wiedemeier *et al.*, 1995). Because ferrous iron reacts with the sulfide produced from the reduction of sulfate, some or most of the ferrous iron may not be observed during groundwater sampling. Some researchers suspect that the observed ferrous iron concentration is much less (10% or less) than the actual amount of ferrous iron that has been generated due to the reactions with other biodegradation products such as H_2S. If this is the case, then the value used for this parameter should be much higher than the observed maximum concentration of ferrous iron in the aquifer.
Typical Values	Data from 28 AFCEE sites: Median = 16.6 mg/L Maximum = 599.5 mg/L Minimum = 0 mg/L
Source of Data	Site monitoring well data. When measuring ferrous iron in the field, the Air

	Force Intrinsic Remediation Technical Protocol (Wiedemeier *et al.*, 1995) can be applied. Enter the average concentration of ferrous iron found in the source zone (see Newell, *et al.*, 1996).
How to Enter Data	Enter directly. This cell will be gray with black text and data may be entered directly only when *Method 2* is chosen, otherwise this cell will be black and locked. A value of zero is used if no data is entered.

PARAMETER	DELTA SULFATE (SO$_4$)
Units	mg/L
Description	This parameter is one component of the total biodegradation capacity of the groundwater as it flows through the source zone and constituent plume. The model assumes that 4.7 mg of sulfate are required to consume 1 mg of BTEX (Wiedemeier *et al.*, 1995).
Typical Values	Data from 28 AFCEE sites: Median = 24.6 mg/L Maximum = 109.2 mg/L Minimum = 0 mg/L
Source of Data	Site monitoring well data. When measuring sulfate in the field, the Air Force Intrinsic Remediation Technical Protocol (Wiedemeier *et al.*, 1995) can be applied. Enter the average background concentration (average upgradient concentration can be used if background information in unavailable) of sulfate minus the lowest observed concentration of sulfate in the source area. The model automatically applies the utilization factor to compute a biodegradation capacity.
How to Enter Data	Enter directly. This cell will be gray with black text and data may be entered directly only when *Method 2* is chosen, otherwise this cell will be black and locked. A value of zero is used if no data is entered.

PARAMETER	OBSERVED METHANE (CH$_4$)
Units	mg/L
Description	This parameter is one component of the total biodegradation capacity of the groundwater as it flows through the source zone and constituent plume. Methane is a metabolic by-product of methanogenic activity. The model assumes that 0.78 mg of methane represents the consumption of 1 mg of BTEX (Wiedemeier *et al.*, 1995).
Typical Values	Data from 28 AFCEE sites: Median = 7.2 mg/L Maximum = 48.4 mg/L Minimum = 0.0 mg/L
Source of Data	Site monitoring well data. When measuring methane in the field, the Air Force Intrinsic Remediation Technical Protocol (Wiedemeier *et al.*, 1995) can be applied. Enter the average observed concentration of methane found in the source area. The model automatically applies the utilization factor to compute a biodegradation capacity.

How to Enter Data	Enter directly. This cell will be gray with black text and data may be entered directly only when *Method 2* is chosen, otherwise this cell will be black and locked. A value of zero is used if no data is entered.

PARAMETER	PERCENTAGE OF BIODEGRADATION CAPACITY
Units	Percent
Description	Amount the total biodegradation capacity must be reduced to account for electron acceptor utilization by other dissolved constituents present in the plume. For example, the calculated biodegradation capacity may be utilized by equal concentrations of benzene, toluene, ethylbenzene, and xylene. If benzene is the modeled constituent in SourceDK, a value of 25% should be entered so that only a portion of the biodegradation capacity is proportioned to benzene. To estimate this value, take the average concentration of the constituent being modeled in the source zone, and divide by the sum of all the other biodegradation dissolved constituents. (For more information, see the BIOSCREEN 1.4 revisions, typically attached to the back of Newell *et al.*, 1996.) As one would expect, this method is an approximation of relatively complex biodegradation processes, and considerable uncertainty is inherent in this calculation.
Typical Values	0 - 100% Default value = 100%
How to Enter Data	Enter directly. This cell will be gray with black text and data may be entered directly only when *Method 2* is chosen, otherwise this cell will be black and locked.

Tier 2 Data Entry:
Time For Output

PARAMETER	NUMBER OF YEARS OVER WHICH TO PLOT DATA
Units	yr
Description	Time period over which concentrations are to be calculated.
Typical Values	1 - 1000 years
Source of Data	From the requirements of the simulation (what the user wants to see).
How to Enter Data	Enter directly.

PARAMETER	TIME IN YEARS WHEN DECAY STARTS
Units	yr
Description	Time from t = 0 at which decay starts. Users can enter this value to simulate long periods when the effect of NAPL caused a long plateau phase for the

	source zone dissolved concentrations, which was then followed by source decay.
Typical Values	0 - 20 years. Default value is 0 yr.
How to Enter Data	Enter directly.

Tier 2 Data Entry: *Uncertainty Range*

PARAMETER	UNCERTAINTY RANGE FOR MASS ESTIMATE
Units	unitless
Description	This is perhaps the most important variable in this model. Users should make a realistic estimate on how much uncertainty is associated with the source mass estimate for the constituent being modeled in SourceDK. For example, for a well-monitored fuel hydrocarbon site, with good density in saturated soil measurements representing constituent concentrations in the NAPL/sorbed compartment, a low-end uncertainty range of ± factor of 2 may be appropriate. This indicates that if the estimated mass for the constituent being modeled is 100 kg, then the model will assume the range in mass estimates is 50 kg to 200 kg. The same level of accuracy (or better) may be achievable using partitioning tracer tests. As a second example, a chlorinated solvent site may have only limited data regarding the possible source mass. A best-guess estimate of 10 kg would be used in the model along with a lower-range estimate of 0.10 kg, and an upper-range estimate of 1000 kg (± factor of 100). The main point of this parameter (and the software to some extent) is that there is a high-level uncertainty in any remediation timeframe estimate, both for natural attenuation remedies and other non-passive remedies such as groundwater pump-and-treat. SourceDK provides a method to evaluate the effect of uncertainty in these estimates.
Typical Values	2 to 100.
How to Enter Data	Enter directly.

Tier 2 Data Entry: *Field Data for Comparison*

PARAMETER	FIELD TIME DATA FOR COMPARISON
Units	yr
Description	The times after t = 0 when concentrations of dissolved organics in wells in the source zone are measured. These data are displayed with model results in the *Show Graph* option.
Typical Values	1 - 10 yr
Source of Data	Monitoring wells located in the source zone.
How to Enter Data	Enter as many or as few years as available after time t = 0. **Enter years in**

	ascending order. Do not leave empty cells between data points. These data are used to calculate the time scale for the plot and compare results.

PARAMETER	FIELD CONCENTRATION DATA FOR COMPARISON
Units	mg/L
Description	Concentration measurements of dissolved organics in wells in the source zone obtained after time t = 0. These data are displayed with model results in the *Show Graph* option.
Typical Values	0.001 - 500 mg/L
Source of Data	Monitoring wells located in the source zone.
How to Enter Data	Enter as many or as few concentration values as available after time t = 0. These data are used only to compare with calculated results.

Tier 2 Data Entry: *Results*

The output shows decay profiles for the dissolved constituent concentration in source. Note that the results are all for the time entered in the *Time for Output* section of the Input screen. The number of years over which to plot data can be changed from this screen as well as the input screen.

The Mini-Calculator allows the user to calculate the concentration of dissolved hydrocarbons in the biodegradation model at a specified time and vice versa.

Analyzing Tier 2 Output: *Concentration Versus Time Chart*

The **Concentration vs. Time Chart** is displayed when the *Show Graph* button is pressed on the *Input* screen. This chart can also be displayed by choosing the *Display Concentration vs. Time Chart* option in the Output screen.

The output screen shows the constituent concentration in the source. The screen shows the concentration profiles for decay without biodegradation or decay with biodegradation, depending on the option selected in the input screen, and the field data. This information is plotted on a linear scale. The user may push the *Log←→Linear* button to see the results on a semi-log plot.

The user can change the number of years over which the decay occurs by:

1. Entering the appropriate number in the Number of Years Over Which to Plot Graph box,
2. Clicking outside the box or hitting Return, and
3. Pressing the Calculate Current Sheet button.

Analyzing Tier 2 Output: *Mass Versus Time Chart*

When the *Display Mass vs. Time Chart* option on the Output screen is chosen, the screen shows the dissolved constituent mass profiles in the source zone. Mass decay profiles with and without biodegradation for the type of field site selected on the Input screen are shown here. This information is plotted on a linear scale. The user may push the *Log←→Linear* button to see the results on a semi-log plot.

The user can change the number of years over which the decay occurs by:

1. Entering the appropriate number in the *Number of Years Over Which to Plot Graph* box,
2. Clicking outside the box or hitting *Return*, and
3. Pressing the *Calculate Current Sheet* button.

Analyzing Tier 2 Output:
Concentration/Time Mini-Calculator

CONCENTRATION (mg/L)
SourceDK calculates the concentration of dissolved constituents at the time specified in the *Time* box of the Mini-Calculator.

The Mini-Calculator accounts for the delay time, if any, entered on the Input screen. Therefore, the concentration calculated by the Mini-Calculator accounts for biodegradation effects only from the decay time. See Appendix A.2.3 for a derivation of the concentration equation.

TIME (yr)
SourceDK calculates the time in years taken by the model to achieve the dissolved constituent concentration value entered in the *Concentration* box of the Mini-Calculator.

Note that the time calculated by the Mini-Calculator is from Time = 0 and not from the delay time entered, if any, on the Input screen. See Appendix A.2.3 for a derivation of the time equation.

TIER 3: PROCESS MODELS

METHOD 1: Dissolved Phase Constituents
METHOD 2: NAPL Zone Constituents
Analyzing Tier 3 Output

Three important considerations regarding data input are:

1) To see the example data set in the input screen of the software, click on the *Paste Example Data Set* button on the lower right portion of the input screen.
2) Because SourceDK is based on the Excel spreadsheet, you have to click outside of the cell where you just entered data or hit *Return* before any of the buttons will work.
3) Parameters used in the model are to be entered directly into the white cells.

The following sequence should be used for viewing the graph:

1. Choose the method to use,
2. Enter value for the parameters, and
3. Press the *Create Graph* button.

Tier 3 Method 1 Data Entry: *Dissolved Phase Constituents*

PARAMETER	ORIGINAL CONSTITUENT CONCENTRATION (C_o)
Units	mg/L
Description	Average concentration of dissolved constituents in wells within the control volume (the area of interest) at time = 0.
Typical Values	0.01 - 500 mg/L
Source of Data	Monitoring well data.
How to Enter Data	Enter directly. Note: This cell will be white with black text and data may be entered directly only when *Method 1* is chosen, otherwise this cell will be gray and locked.

PARAMETER	DESIRED CLEANUP LEVEL (C_t)
Units	mg/L
Description	Desired clean-up level for the constituent.
Source of Data	Regulatory agencies, such as MCLs or Protective Concentration Levels, or values derived from risk assessments.
How to Enter Data	Enter directly. Note: This cell will be white with black text and data may be entered directly only when *Method 1* is chosen, otherwise this cell will be gray and locked.

PARAMETER	LENGTH OF SOURCE ZONE PARALLEL TO GROUNDWATER FLOW (L)
Units	ft
Description	Length of plume along flow path in control volume parallel to the groundwater flow. Note that the control volume (the portion of plume of interest) must be outside the influence of any sources such as non-aqueous phase liquids, but can be influenced by sorption of dissolved constituents on the aquifer material.
Typical Values	10 - 1000 ft
Source of Data	Maps of dissolved-phase plume.
How to Enter Data	Enter directly. Note: This cell will be white with black text and data may be entered directly only when *Method 1* is chosen, otherwise this cell will be gray and locked.

PARAMETER	GROUNDWATER SEEPAGE VELOCITY (V_s)
Units	ft/yr

Description	Actual interstitial groundwater velocity, equaling Darcy velocity divided by effective porosity. Note that SourceDK is not formulated to simulate the effects of chemical diffusion. Therefore, constituent transport through very slow hydrogeologic regimes (e.g., clays and slurry walls) should probably not be modeled using SourceDK unless the effects of chemical diffusion are proven to be insignificant. Domenico and Schwartz (1990) indicate that chemical diffusion is insignificant for Peclet numbers (seepage velocity times median pore size divided by the bulk diffusion coefficient) > 100.
Typical Values	1 to 1500 ft/yr
Source of Data	Calculated by multiplying hydraulic conductivity by hydraulic gradient and dividing by effective porosity ($V_s = (K * i) / n_e$). It is strongly recommended that actual site data be used for hydraulic conductivity and hydraulic gradient data parameters; effective porosity can be estimated.
How to Enter Data	Enter directly. Note: This cell will be white with black text and data may be entered directly only when *Method 1* is chosen, otherwise this cell will be gray and locked.

PARAMETER	RETARDATION FACTOR (R)
Units	Unitless
Description	The retardation factor is the ratio of the dissolved plume sorbed constituent mass to the dissolved constituent mass in the aqueous phase in a unit volume of the aquifer. The retardation factor is a function of both aquifer and constituent properties.
Typical Values	1-3 (typical for BTEX) 2-5 (typical for chlorinated solvents)
Source of Data	Usually estimated from soil and chemical data using the following expression: $R = 1 + K_d \cdot \rho_d / n$ where $K_d = K_{oc} \cdot f_{oc}$ where ρ_d = bulk density, n = porosity, K_{oc} = organic carbon-water partition coefficient, K_d = distribution coefficient, and f_{oc} = fraction organic carbon on uncontaminated soil. In some cases, the retardation factor can be estimated by comparing the length of a plume affected by adsorption (such as the benzene plume) with the length of plume that is not affected by adsorption (such as chloride). Most plumes do not have both types of constituents, so it is more common to use the estimation technique.
How to Enter Data	1) Enter directly, or 2) Enter data in the gray cells and press *Calculate R*. Note: This cell will be white with black text and data may be entered directly only when *Method 1* is chosen, otherwise this cell will be gray and locked.

PARAMETER	SOIL BULK DENSITY (ρ or rho)
Units	kg/L or g/cc
Description	Density of the saturated aquifer material (referred to as "soil"), excluding soil moisture.
Typical Values	Although this value can be measured in the lab, in most cases estimated values are used. A value of 1.7 kg/L is used frequently.
Source of Data	Either from an analysis of soil samples at a geotechnical lab or more commonly, application of estimated values such as 1.7 kg/L.
How to Enter Data	Enter directly in gray cell. This parameter is not needed if the Retardation factor is entered directly. Note: This cell will be white with black text and data may be entered directly only when *Method 1* is chosen, otherwise this cell will be gray and locked.

PARAMETER	PARTITION COEFFICIENT (K_{oc})
Units	L/kg
Description	Chemical-specific partition coefficient between soil organic carbon and the aqueous phase. Larger values indicate greater affinity of organic constituents for the organic carbon fraction of soil. This value is chemical specific and can be found in chemical reference books. Note that many users of SourceDK will simulate BTEX as a single constituent. In this case, either an average value for the BTEX compounds can be used, or it can be assumed that all of the BTEX compounds have the same mobility as benzene (the constituent with the highest potential risk to human health).
Typical Values	Benzene 38 L/kg Perchloroethylene 426 L/kg Ethylbenzene 95 L/kg Trichloroethylene 130 L/kg Toluene 135 L/kg Dichloroethylene 125 L/kg Xylene 240 L/kg Vinyl Chloride 29.6 L/kg (ASTM, 1995) (Aziz *et al.*, 2000) (Note that there is a wide range of reported values; for example, Mercer and Cohen (1990) report a K_{oc} for benzene of 83 L/kg.) For more information see Pankow and Cherry, 1996 (for solvents) and Wiedemeier *et al.*, 1999 (variety of constituents).
Source of Data	Chemical reference literature such as Pankow and Cherry, 1996 (for solvents); Wiedemeier *et al.*, 1999 (variety of constituents); or other references with chemical properties. Alternatively one can use relationships between K_{oc} and solubility or K_{oc} and the octanol-water partition coefficient (K_{ow}) to determine K_{oc}.
How to Enter Data	Enter directly in gray cell. This parameter is not needed if the Retardation factor is entered directly. Note: This cell will be white with black text and data may be entered directly only when *Method 1* is chosen, otherwise this cell will be gray and locked.

PARAMETER	FRACTION ORGANIC CARBON (f_{oc})
Units	Unitless
Description	Fraction of the aquifer material comprised of natural organic carbon in uncontaminated areas. More natural organic carbon means higher adsorption of organic constituents on the aquifer matrix.
Typical Values	0.0002 - 0.02
Source of Data	The fraction organic carbon value should be measured, if possible, by collecting a sample of aquifer material from an uncontaminated saturated zone and performing a laboratory analysis (e.g. ASTM Method 2974-87 or equivalent). If unknown, a default value of 0.001 is often used (e.g., ASTM 1995).
How to Enter Data	Enter directly in gray cell. This parameter is not needed if the Retardation factor is entered directly. Note: This cell will be white with black text and data may be entered directly only when *Method 1* is chosen, otherwise this cell will be gray and locked.

PARAMETER	EFEECTIVE POROSITY (n_e)
Units	Unitless
Description	Dimensionless ratio of the volume of interconnected voids to the bulk volume of the aquifer matrix. Note that *total porosity* is the ratio of all voids (including non-connected voids) to the bulk volume of the aquifer matrix. Difference between total and effective porosity reflect lithologic controls on pore structure. In unconsolidated sediments coarser than silt size, effective porosity can be less than total porosity by 2-5% (e.g. 0.28 vs. 0.30) (Smith and Wheatcraft, 1993).
Typical Values	Values for Effective Porosity: Clay 0.01 - 0.20 Sandstone 0.005 - 0.10 Silt 0.01 - 0.30 Gravel 0.10 - 0.35 Fract. Granite 0.00005 - 0.01 Unfract. Limestone 0.001 - 0.05 Fine Sand 0.10 - 0.30 Medium Sand 0.15 - 0.30 Coarse Sand 0.20 - 0.35 (From Wiedemeier *et al.*, 1999, originally from Domenico and Schwartz, 1990, and Walton, 1988).
Source of Data	Typically estimated. The ASTM RBCA Standard (ASTM, 1995) includes a default value of 0.38 (to be used primarily for unconsolidated deposits).
How to Enter Data	Enter directly in gray cell. This parameter is not needed if the Retardation factor is entered directly. Note: This cell will be blue with black text and data may be entered directly only when *Method 1* is chosen, otherwise this cell will be gray and locked.

Tier 3 Method 2 Data Entry: NAPL Zone Constituents

PARAMETER	TYPE OF MEDIA
Description	A general description of how well sorted the aquifer material is. This process model is based on the assumption that the amount of NAPL trapped in a media is related to the changes in the surface area of the dissolving NAPL blob (Powers *et al.*, 1994).
	The user can choose *uniform media* or *well-graded* (non-uniform) media. Coarse sand corresponds to a hydraulic conductivity of 10^{-2} cm/s, fine sand corresponds to a hydraulic conductivity of 10^{-3} cm/s, and silty sand corresponds to a hydraulic conductivity of 10^{-4} cm/s.

PARAMETER	INITIAL AQUEOUS-PHASE CONCENTRATION IN SOURCE ZONE (C_s)
Units	mg/L
Description	Average concentration of dissolved constituents in wells within the control volume (the area of interest) at time = 0. For this model, the control volume must contain NAPL.
Typical Values	0.01 - 500 mg/L
Source of Data	Monitoring well data.
How to Enter Data	Enter directly.
	Note: This cell will be white with black text and data may be entered directly only when *Method 2* is chosen, otherwise this cell will be gray and locked.

PARAMETER	DESIRED CLEANUP LEVEL (C_t)
Units	mg/L
Description	Desired cleanup level for the constituent.
Source of Data	Regulatory agencies, such as MCLs or Protective Concentration Levels, or values derived from risk assessments.
How to Enter Data	Enter directly.
	Note: This cell will be white with black text and data may be entered directly only when *Method 2* is chosen, otherwise this cell will be gray and locked.

PARAMETER	DENSITY NAPL FLUID (Rho)
Units	g/cm^3
Description	Density of the source NAPL.
Typical Values	0.80 to 1.4
Source of Data	From an analysis of NAPL samples or estimated.
How to Enter Data	Enter directly.

| | Note: This cell will be white with black text and data may be entered directly only when *Method 2* is chosen, otherwise this cell will be gray and locked. |

PARAMETER	INITIAL NAPL SATURATION IN POROUS MEDIA (S$_o$)
Units	Percent
Description	An estimate of how much of the pore space is filled with Non-Aqueous Phase Liquids (NAPL).
Typical Values	0 – 30. For a discussion of saturation at solvent sites, see Pankow and Cherry, 1996. For a detailed discussion of solvents and fuels, see Mercer and Cohen, 1990. For a brief summary see Chapter 2 of Wiedemeier *et al.*, 1999.
Source of Data	This value can be measured by analyzing soil samples. Without site specific measurements estimates will likely be an order-of-magnitude or greater inaccurate.
How to Enter Data	Enter directly. Note: This cell will be white with black text and data may be entered directly only when *Method 2* is chosen, otherwise this cell will be gray and locked.

PARAMETER	UNCERTAINTY IN NAPL SATURATION
Units	Unitless
Description	This is perhaps the most important variable in this model. Users should make a realistic estimate on how much uncertainty is associated with the estimation of the NAPL saturation being modeled in SourceDK. For example, for a well-monitored fuel hydrocarbon site, with good density in saturated soil measurements representing constituent concentrations in the saturated NAPL compartment, a low-end uncertainty range of ± factor of 2 may be appropriate. This indicates that if the estimated NAPL saturation for the constituent being modeled is 10%, then the model will assume the range in NAPL saturation is 5 % to 20 %. The main point of this parameter (and the software to some extent) is that there is a high-level uncertainty in any remediation timeframe estimate, both for natural attenuation remedies and other non-passive remedies such as groundwater pump-and-treat. SourceDK provides a method to evaluate the effect of uncertainty in these estimates.
Typical Values	2 to 100.
How to Enter Data	Enter directly. Note: This cell will be white with black text and data may be entered directly only when *Method 2* is chosen, otherwise this cell will be gray and locked.

PARAMETER	NATURAL GROUNDWATER SEEPAGE VELOCITY (V$_s$)
Units	ft/yr
Description	Actual interstitial groundwater velocity, equaling Darcy velocity divided by effective porosity for natural (non-pumping) conditions in aquifer. Note that

	SourceDK is not formulated to simulate the effects of chemical diffusion. Therefore, contaminant transport through very slow hydrogeologic regimes (e.g., clays and slurry walls) should probably not be modeled using SourceDK unless the effects of chemical diffusion are proven to be insignificant. Domenico and Schwartz (1990) indicate that chemical diffusion is insignificant for Peclet numbers (seepage velocity times median pore size divided by the bulk diffusion coefficient) > 100.
Typical Values	1 to 1500 ft/yr
Source of Data	Calculated by multiplying hydraulic conductivity by hydraulic gradient and dividing by effective porosity (Vs = (K * i)/ne). It is strongly recommended that actual site data be used for hydraulic conductivity and hydraulic gradient data parameters; effective porosity can be estimated.
How to Enter Data	Enter directly. Note: This cell will be white with black text and data may be entered directly only when *Method 2* is chosen, otherwise this cell will be gray and locked.

PARAMETER	LENGTH OF SOURCE ZONE PARALLEL TO GROUNDWATER FLOW (L)
Units	ft
Description	Length of plume along flow path in control volume parallel to the groundwater flow. The control volume must be a NAPL-affected zone (either continuous phase or residual NAPL). Note that at many or most NAPL zones the NAPL is never directly observed; see Pankow and Cherry, 1996 and Wiedemeier *et al.*, 1999.
Typical Values	10 - 1000 ft
Source of Data	Maps of extent of NAPL-affected zone.
How to Enter Data	Enter directly. Note: This cell will be white with black text and data may be entered directly only when *Method 2* is chosen, otherwise this cell will be gray and locked.

PARAMETER	IS THIS A PUMPING SCENARIO?
Description	Employing the use of a pump in the source zone results in mass transfer effects. This changes the number of pore volumes required to remediate the source zone.
How to Enter Data	Select *Yes* or *No*. If *Yes* is selected then the user is prompted to provide a value for the typical groundwater seepage velocity while pumping. Note: This option is available only when *Method 2* is chosen.

PARAMETER	TYPICAL GROUNDWATER SEEPAGE VELOCITY WHILE PUMPING
Units	ft/yr
Description	Average groundwater seepage velocity in control volume while pumping.
Typical Values	1 to 3000 ft/yr

Source of Data	Calculations using hydraulic conductivity and the potentiometric surface maps from a period when pumping was on-going. A second, more general method is to estimate the discharge through the control volume without pumping (in units of volume per time), and then compare this value to the total pumping rate (in units of volume per time). Then increase the natural groundwater seepage velocity by the ratio of the pumping rate to the natural discharge rate.
How to Enter Data	Enter directly. Note: This cell will be white with black text and data may be entered directly only when *Method 2 Pumping Scenario Yes* is chosen, otherwise this cell will be gray and locked.

Analyzing Tier 3 Output

PARAMETER	GRAPH OUTPUT
Description	The plot of concentration versus time data is plotted on a semi-logarithmic scale. The model calculates the date when the desired clean-up level for the method chosen will be reached. For NAPL zone constituents, SourceDK also plots the uncertainties in the estimation.
How to Enter Data	Click on the *Create Graph* button to create and update graph.

PARAMETER	NUMBER OF PORE VOLUMES (PV)
Description	A pore volume is the volume of water required to replace water in a unit volume of saturated porous media. Note that the concept of pore volume does not mean that all of the water originally in the porous media is removed and replaced by clean water; one pore volume is the volume of water that actually flows through the porous media.
	Method 1 for dissolved phase constituents uses the Simple Flushing Model (Newell *et al.*, 1994) to calculate the pore volumes.
	Method 2 for NAPL zone constituents uses a simplified version (Newell *et al.*, 1994) of the Theta Model (Powers *et al.*, 1994) to calculate the number of pore volumes.

PARAMETER	TIME TO FLUSH OUT CONSTITUENTS
Description	The time required to flush out the constituents from the source zone, after accounting for the presence of NAPL.

For pumping scenarios this intermediate output value is displayed:

PARAMETER	CONCENTRATION IN PRODUCED GROUNDWATER
Units	mg/L
Description	Initial aqueous-phase concentration while pumping, as impacted by mass transfer effects, prior to flushing.
	Note that this model is very sensitive to Cs; the user should make certain that the residual saturation value represents the same scale as the initial aqueous-phase concentration. In other words, if a field value of Cs is used (i.e., the concentrations observed in pumping wells), one should ensure that the residual saturation represents the actual field conditions.
	See Appendix A.4.3 for a description of how mass transfer effects are included in SourceDK for pumping scenarios.
Typical Values	0.01 - 50 mg/L
Source of Data	Monitoring wells located near the centerline of the plume.
How to Enter Data	This value is calculated automatically therefore the cell is black and locked.
	Note: This option is available only when *Method 2 Pumping Scenario Yes* is chosen, otherwise this cell will be gray and locked.

BACKGROUND INFORMATION FOR SourceDK MODELING

Source Decay Database and Source Decay Rate Constants at Field Sites

Source decay rate constants (k_s) and the associated half lives were derived for chlorinated solvents and petroleum fuel by analyzing two plume databases: 1) a database of underground storage tank sites in Texas developed by Mace (1997); and 2) a chlorinated solvent database developed by McNab *et al*. (1999) and McNab (2001). Shrinking, expanding, and stable plumes were all considered in the analysis, however, only the wells with at least three years of monitoring data were retained. The analysis was further screened as

- Case A, where both the source and plume wells were considered;
- Case B, where only the source wells were considered;
- Case C, where only low concentration source wells were evaluated;
- Case D, where only low concentration source wells were evaluated.

For petroleum hydrocarbon sites, the constituents of interest were benzene, toluene, ethylbenzene, xylenes, and methyl tertiary-butyl ether (MTBE). While for chlorinated solvent sites, tetrachloroethylene (PCE), trichloroethylene (TCE), cis-1,2-dichloroethylene (cis-1,2-DCE), vinyl chloride (VC), 1,2-dichloroethane (1,2-DCA), and 1,1,1- trichloroethane (1,1,1-TCA) were investigated. Wells for each constituent were analyzed independent of the presence of other constituents.

Methodology

The primary objective of this analysis was to obtain source lifetime information. For this purpose, data from shrinking, expanding, and stable plumes were all considered in the analysis. Procedures for data analysis included the following:

1) A database of underground storage tank sites in Texas developed by Mace (1997) was used in the derivation of hydrocarbon fuel source decay rates. While a database developed by McNab *et al*. (1999) and McNab (2001) was used in the derivation of source decay rates for chlorinated solvent plumes.

2) Wells with at least 3 years of monitoring data were selected for analysis. The analysis was further screened as follows:
   a) **Case A:** Source and Plume Wells
      i) All wells at the site were considered in the derivation of k_s.
   b) **Case B:** Source Wells
      i) Only the well with the highest concentration at each site was used to derive k_s.
   c) **Case C:** Source Wells from High Concentration Sites
      i) Only the well with the highest concentration at each site was used.
      ii) The median value of the concentrations from all the sites was determined.
      iii) k_s values were determined using only the wells with concentrations *greater* than the median concentration.
   d) **Case D:** Source Wells from Low Concentration Sites
      i) Only the well with the highest concentration at each site was used.

ii) The median value of the concentration for these sites was determined.

iii) k_s values were determined using only the wells with concentrations *smaller* than the median concentration.

3) For hydrocarbon fuel sites, the constituents of interest were benzene, toluene, ethylbenzene, xylenes, and MTBE. While for chlorinated solvent sites, PCE, TCE, cis-1,2-DCE, VC, 1,2-DCA, and 1,1,1-TCA were investigated. Wells for each constituent were analyzed independent of the presence of other constituents.

4) Source decay rates were derived by linearly regressing the natural logarithm of concentration against time. Shrinking plumes were represented with a positive k_s, while expanding plumes with a negative k_s.

5) Regression correlation coefficients were calculated.

6) The maximum, 95th percentile, 75th percentile, median, 25th percentile, 10th percentile, and minimum k_s values for each case were obtained for each constituent. Additionally, the median concentration and regression correlation were also determined.

7) Source half-lives were determined for each k_s determined above.

Typical Source Decay Constants at Field Sites

For petroleum hydrocarbons, 366 sites with 1,775 wells were analyzed to develop the database. A total of 40 sites with 1,109 wells were analyzed for chlorinated solvents. Table 1 summarizes decay rate constants and half-lives for fuel sites, while Table 2 summarizes the results of chlorinated solvent sites. Figure 7 shows the graphical representation of k_s for Case B for petroleum hydrocarbon sites while Figure 8 shows the k_s for chlorinated solvent sites.

These values can be used as typical source decay values from leaking underground storage sites and from chlorinated solvent sites. Users should be cautioned that actual source decay rate constants may differ significantly from the distributions developed from this analysis.

Table 1: Source Decay Rate Constants (k$_s$) and Source Decay Half-Lives from Petroleum Fuel Site Database

	CASE A: Source Wells Lumped Together With Plume Wells														
	Benzene			**Toluene**			**Ethylbenzene**			**Xylenes**			**MTBE**		
	k$_s$ l/yr	Source Trend	Half Life yr	k$_s$ l/yr	Source Trend	Half Life yr	k$_s$ l/yr	Source Trend	Half Life yr	k$_s$ l/yr	Source Trend	Half Life yr	k$_s$ l/yr	Source Trend	Half Life yr
Maximum	-3.15	Expanding	NA	-2.39	Expanding	NA	-2.07	Expanding	NA	-2.18	Expanding	NA	-4.47	Expanding	NA
90 Percentile	-0.40	Expanding	NA	-0.25	Expanding	NA	-0.37	Expanding	NA	-0.34	Expanding	NA	-0.90	Expanding	NA
75 Percentile	-0.05	Expanding	NA	0.06	Shrinking	NA	-0.05	Expanding	NA	-0.04	Expanding	NA	-0.39	Expanding	NA
50 Percentile	**0.28**	**Shrinking**	**2.47**	**0.43**	**Shrinking**	**1.62**	**0.21**	**Shrinking**	**3.27**	**0.25**	**Shrinking**	**2.71**	**-0.02**	**Expanding**	**NA**
25 Percentile	0.70	Shrinking	0.99	0.83	Shrinking	0.84	0.60	Shrinking	1.15	0.64	Shrinking	1.09	0.50	Shrinking	1.38
10 Percentile	1.23	Shrinking	0.56	1.36	Shrinking	0.51	1.05	Shrinking	0.66	1.19	Shrinking	0.58	0.90	Shrinking	0.77
Minimum	4.75	Shrinking	0.15	6.42	Shrinking	0.11	4.43	Shrinking	0.16	7.10	Shrinking	0.10	6.90	Shrinking	0.10
Median r^2	0.30			0.38			0.28			0.30			0.35		
Median conc (mg/L)	2.00			1.20			0.88			2.65			0.50		
Total no. of sites	359		359	89		89	90		90	89		89	78		78
Total no. of wells	1,438		1,438	480		480	453		453	480		480	213		213

	CASE B: Source Wells Only (Only Highest Concentration Well at Each Site)														
	Benzene			**Toluene**			**Ethylbenzene**			**Xylenes**			**MTBE**		
	k$_s$ l/yr	Source Trend	Half Life yr	k$_s$ l/yr	Source Trend	Half Life yr	k$_s$ l/yr	Source Trend	Half Life yr	k$_s$ l/yr	Source Trend	Half Life yr	k$_s$ l/yr	Source Trend	Half Life yr
Maximum	-3.02	Expanding	NA	-2.39	Expanding	NA	-1.66	Expanding	NA	-2.18	Expanding	NA	-4.47	Expanding	NA
90 Percentile	-0.30	Expanding	NA	-0.26	Expanding	NA	-0.44	Expanding	NA	-0.37	Expanding	NA	-1.28	Expanding	NA
75 Percentile	-0.07	Expanding	NA	0.003	Shrinking	260.43	-0.15	Expanding	NA	-0.09	Expanding	NA	-0.38	Expanding	NA
50 Percentile	**0.22**	**Shrinking**	**3.12**	**0.41**	**Shrinking**	**1.71**	**0.18**	**Shrinking**	**3.76**	**0.25**	**Shrinking**	**2.77**	**0.08**	**Shrinking**	**8.19**
25 Percentile	0.65	Shrinking	1.07	0.96	Shrinking	0.73	0.69	Shrinking	1.01	0.66	Shrinking	1.05	0.62	Shrinking	1.12
10 Percentile	1.37	Shrinking	0.51	1.56	Shrinking	0.44	1.32	Shrinking	0.52	1.43	Shrinking	0.48	1.37	Shrinking	0.51
Minimum	4.49	Shrinking	0.15	6.42	Shrinking	0.11	2.96	Shrinking	0.23	7.10	Shrinking	0.10	6.90	Shrinking	0.10
Median r^2	0.31			0.35			0.30			0.30			0.34		
Median conc (mg/L)	5.90			9.70			2.50			11.00			1.40		
Total no. of sites	359		359	89		89	90		90	89		89	78		78

NOTE: The Source Decay Rate Constant (k$_s$) is used in a first-order decay relationship to describe how quickly the dissolved concentrations in the source zone (i.e., concentrations that are directly controlled by the rate of NAPL dissolution and/or the rate of desorption from the aquifer material) decline over time. This rate constant **is not** the same rate constant that represents the attenuation of dissolved-phase constituents that have left the source zone (k) or the biodegradation of dissolved constituents (λ). See Appendix A.1 for more information. Median concentration represents the median of the maximum concentration at each well. NA = Not Applicable.

Table 1: Source Decay Rate Constants (k$_s$) and Source Decay Half-Lives from Petroleum Fuel Site Database Cont'd

	CASE C: Source Wells With High Concentrations (Concentrations > Median Concentrations from Source Well Database)														
	Benzene			Toluene			Ethylbenzene			Xylenes			MTBE		
	k$_s$ l/yr	Source Trend	Half Life yr	k$_s$ l/yr	Source Trend	Half Life yr	k$_s$ l/yr	Source Trend	Half Life yr	k$_s$ l/yr	Source Trend	Half Life yr	k$_s$ l/yr	Source Trend	Half Life yr
Maximum	-3.02	Expanding	NA	-1.47	Expanding	NA	-1.66	Expanding	NA	-1.59	Expanding	NA	-4.47	Expanding	NA
90 Percentile	-0.27	Expanding	NA	-0.22	Expanding	NA	-0.42	Expanding	NA	-0.30	Expanding	NA	-1.24	Expanding	NA
75 Percentile	-0.09	Expanding	NA	0.13	Shrinking	5.49	-0.09	Expanding	NA	-0.03	Expanding	NA	0.001	Shrinking	742.93
50 Percentile	**0.16**	**Shrinking**	**4.31**	**0.44**	**Shrinking**	**1.57**	**0.22**	**Shrinking**	**3.22**	**0.25**	**Shrinking**	**2.75**	**0.46**	**Shrinking**	**1.52**
25 Percentile	0.53	Shrinking	1.31	1.12	Shrinking	0.62	0.70	Shrinking	0.98	0.64	Shrinking	1.09	0.80	Shrinking	0.87
10 Percentile	1.13	Shrinking	0.61	2.47	Shrinking	0.28	1.25	Shrinking	0.55	1.68	Shrinking	0.41	2.01	Shrinking	0.34
Minimum	4.49	Shrinking	0.15	6.42	Shrinking	0.11	2.77	Shrinking	0.25	7.10	Shrinking	0.10	3.26	Shrinking	0.21
Median r^2	0.24			0.31			0.36			0.23			0.34		
Median conc (mg/L)	13.46			27.00			6.03			19.35			9.40		
Total no. of sites	180		180	45		45	48		48	46		46	39		39

	CASE D: Source Wells With Low Concentrations (Concentrations < Median Concentrations from Source Well Database)														
	Benzene			Toluene			Ethylbenzene			Xylenes			MTBE		
	k$_s$ l/yr	Source Trend	Half Life yr	k$_s$ l/yr	Source Trend	Half Life yr	k$_s$ l/yr	Source Trend	Half Life yr	k$_s$ l/yr	Source Trend	Half Life yr	k$_s$ l/yr	Source Trend	Half Life yr
Maximum	-1.32	Expanding	NA	-2.39	Expanding	NA	-1.38	Expanding	NA	-2.18	Expanding	NA	-2.01	Expanding	NA
90 Percentile	-0.39	Expanding	NA	-0.35	Expanding	NA	-0.45	Expanding	NA	-0.39	Expanding	NA	-1.25	Expanding	NA
75 Percentile	-0.05	Expanding	NA	-0.04	Expanding	NA	-0.17	Expanding	NA	-0.20	Expanding	NA	-0.61	Expanding	NA
50 Percentile	**0.30**	**Shrinking**	**2.33**	**0.38**	**Shrinking**	**1.81**	**0.16**	**Shrinking**	**4.39**	**0.19**	**Shrinking**	**3.72**	**-0.20**	**Expanding**	**NA**
25 Percentile	0.79	Shrinking	0.88	0.94	Shrinking	0.73	0.66	Shrinking	1.05	0.68	Shrinking	1.02	0.19	Shrinking	3.72
10 Percentile	1.45	Shrinking	0.48	1.30	Shrinking	0.53	1.46	Shrinking	0.48	1.33	Shrinking	0.52	0.94	Shrinking	0.74
Minimum	4.38	Shrinking	0.16	5.54	Shrinking	0.13	2.96	Shrinking	0.23	2.92	Shrinking	0.24	6.90	Shrinking	0.10
Median r^2	0.36			0.43			0.28			0.34			0.34		
Median conc (mg/L)	2.20			3.08			0.98			5.60			0.09		
Total no. of sites	179		179	44		44	42		42	43		43	39		39

NOTE: The Source Decay Rate Constant (k$_s$) is used in a first-order decay relationship to describe how quickly the dissolved concentrations in the source zone (i.e., concentrations that are directly controlled by the rate of NAPL dissolution and/or the rate of desorption from the aquifer material) decline over time. This rate constant **is not** the same rate constant that represents the attenuation of dissolved-phase constituents that have left the source zone (k) or the biodegradation of dissolved constituents (λ). See Appendix A.1 for more information. Median concentration represents the median of the maximum concentration at each well. NA = Not Applicable.

Table 2: Source Decay Rate Constants (k_s) and Source Decay Half-Lives from Chlorinated Solvent Site Database

CASE A: Source Wells Lumped Together With Plume Wells																	
	PCE			TCE			cis-DCE			VC			12-DCA			111-TCA		
	k_s l/yr	Source Trend	$t_{1/2}$ yr	k_s l/yr	Source Trend	$t_{1/2}$ yr	k_s l/yr	Source Trend	$t_{1/2}$ yr	k_s l/yr	Source Trend	$t_{1/2}$ yr	k_s l/yr	Source Trend	$t_{1/2}$ yr	k_s l/yr	Source Trend	$t_{1/2}$ yr
Maximum	-3.93	Expanding	NA	-2.94	Expanding	NA	-0.93	Expanding	NA	-1.17	Expanding	NA	-3.93	Expanding	NA	-1.86	Expanding	NA
90 Percentile	-0.39	Expanding	NA	-0.30	Expanding	NA	-0.39	Expanding	NA	-0.46	Expanding	NA	-0.29	Expanding	NA	-0.29	Expanding	NA
75 Percentile	-0.15	Expanding	NA	-0.09	Expanding	NA	-0.11	Expanding	NA	-0.26	Expanding	NA	-0.15	Expanding	NA	-0.01	Expanding	NA
50 Percentile	**0.03**	**Shrinking**	**24.50**	**0.08**	**Shrinking**	**8.30**	**0.11**	**Shrinking**	**6.27**	**-0.03**	**Expanding**	**NA**	**0.02**	**Shrinking**	**35.66**	**0.18**	**Shrinking**	**3.88**
25 Percentile	0.23	Shrinking	3.08	0.27	Shrinking	2.58	0.36	Shrinking	1.94	0.16	Shrinking	4.22	0.21	Shrinking	3.29	0.34	Shrinking	2.01
10 Percentile	0.60	Shrinking	1.15	0.54	Shrinking	1.29	0.67	Shrinking	1.03	0.45	Shrinking	1.55	0.46	Shrinking	1.50	0.59	Shrinking	1.17
Minimum	2.19	Shrinking	0.32	3.66	Shrinking	0.19	2.39	Shrinking	0.29	1.44	Shrinking	0.48	1.25	Shrinking	0.55	2.81	Shrinking	0.25
Median r^2	0.26			0.38			0.29			0.31			0.22			0.40		
Median conc (mg/L)	0.01			0.05			0.01			0.08			0.01			0.02		
Total no. of sites	32			37			11			18			13			23		
Maximum	325			910			112			226			144			301		

CASE B: Source Wells Only (Only Highest Concentration Well at Each Site)																	
	PCE			TCE			cis-DCE			VC			12-DCA			111-TCA		
	k_s l/yr	Source Trend	$t_{1/2}$ yr	k_s l/yr	Source Trend	$t_{1/2}$ yr	k_s l/yr	Source Trend	$t_{1/2}$ yr	k_s l/yr	Source Trend	$t_{1/2}$ yr	k_s l/yr	Source Trend	$t_{1/2}$ yr	k_s l/yr	Source Trend	$t_{1/2}$ yr
Maximum	-3.93	Expanding	NA	-1.43	Expanding	NA	-0.22	Expanding	NA	-1.17	Expanding	NA	-3.93	Expanding	NA	-1.06	Expanding	NA
90 Percentile	-0.39	Expanding	NA	-0.59	Expanding	NA	-0.10	Expanding	NA	-0.50	Expanding	NA	-0.19	Expanding	NA	-0.30	Expanding	NA
75 Percentile	-0.14	Expanding	NA	-0.16	Expanding	NA	0.14	Shrinking	5.04	-0.04	Expanding	NA	-0.02	Expanding	NA	-0.06	Expanding	NA
50 Percentile	**0.11**	**Shrinking**	**6.16**	**0.15**	**Shrinking**	**4.65**	**0.62**	**Shrinking**	**1.12**	**0.07**	**Shrinking**	**10.53**	**0.14**	**Shrinking**	**4.94**	**0.15**	**Shrinking**	**4.51**
25 Percentile	0.51	Shrinking	1.37	0.27	Shrinking	2.53	0.78	Shrinking	0.89	0.45	Shrinking	1.53	0.51	Shrinking	1.37	0.36	Shrinking	1.95
10 Percentile	0.78	Shrinking	0.89	0.72	Shrinking	0.96	0.98	Shrinking	0.71	1.02	Shrinking	0.68	0.67	Shrinking	1.03	0.67	Shrinking	1.03
Minimum	1.84	Shrinking	0.38	2.42	Shrinking	0.29	1.75	Shrinking	0.40	1.44	Shrinking	0.48	1.25	Shrinking	0.55	1.50	Shrinking	0.46
Median r^2	0.28			0.21			0.47			0.33			0.48			0.32		
Median conc (mg/L)	0.13			1.76			1.67			0.40			0.10			0.24		
Total no. of sites	32		32	37		37	11		11	18		18	13		13	23		23

NOTE: The Source Decay Rate Constant (k_s) is used in a first-order decay relationship to describe how quickly the dissolved concentrations in the source zone (i.e., concentrations that are directly controlled by the rate of NAPL dissolution and/or the rate of desorption from the aquifer material) decline over time. This rate constant **is not** the same rate constant that represents the attenuation of dissolved-phase constituents that have left the source zone (k) or the biodegradation of dissolved constituents (λ). See Appendix A.1 for more information. Median concentration represents the median of the maximum concentration at each well. NA = Not Applicable.

Table 2: Source Decay Rate Constants (k$_s$) and Source Decay Half-Lives from Chlorinated Solvent Site Database (cont'd)

	CASE C: Source Wells With High Concentrations (Concentrations > Median Concentrations from Source Well Database)

	\multicolumn{3}{c}{PCE}	\multicolumn{3}{c}{TCE}	\multicolumn{3}{c}{cis-DCE}	\multicolumn{3}{c}{VC}	\multicolumn{3}{c}{12-DCA}	\multicolumn{3}{c}{111-TCA}
	k$_s$ l/yr	Source Trend	t$_{1/2}$ yr	k$_s$ l/yr	Source Trend	t$_{1/2}$ yr	k$_s$ l/yr	Source Trend	t$_{1/2}$ yr	k$_s$ l/yr	Source Trend	t$_{1/2}$ yr	k$_s$ l/yr	Source Trend	t$_{1/2}$ yr	k$_s$ l/yr	Source Trend	t$_{1/2}$ yr
Maximum	0.04	Shrinking	15.98	-0.18	Expanding	NA	-0.22	Expanding	NA	-1.17	Expanding	NA	-0.17	Expanding	NA	-1.06	Expanding	NA
90 Percentile	0.09	Shrinking	7.92	-0.09	Expanding	NA	-0.17	Expanding	NA	-0.94	Expanding	NA	-0.07	Expanding	NA	-0.85	Expanding	NA
75 Percentile	0.13	Shrinking	5.20	0.06	Shrinking	10.84	-0.10	Expanding	NA	-0.18	Expanding	NA	0.06	Shrinking	10.89	0.12	Shrinking	6.01
50 Percentile	**0.50**	**Shrinking**	**1.40**	**0.18**	**Shrinking**	**3.84**	**0.81**	**Shrinking**	**0.86**	**-0.03**	**Expanding**	**NA**	**0.30**	**Shrinking**	**2.31**	**0.31**	**Shrinking**	**2.21**
25 Percentile	0.77	Shrinking	0.90	0.27	Shrinking	2.54	0.98	Shrinking	0.71	0.42	Shrinking	1.63	0.52	Shrinking	1.33	0.59	Shrinking	1.17
10 Percentile	0.84	Shrinking	0.83	0.69	Shrinking	1.01	1.44	Shrinking	0.48	1.31	Shrinking	0.53	0.63	Shrinking	1.09	0.69	Shrinking	1.01
Minimum	1.20	Shrinking	0.58	2.42	Shrinking	0.29	1.75	Shrinking	0.40	1.44	Shrinking	0.48	0.71	Shrinking	0.98	1.01	Shrinking	0.69
Median r^2	0.26			0.10			0.56			0.42			0.33			0.38		
Median conc (mg/L)	2.60			47.00			0.14			0.79			2.15			22.80		
Total no. of sites	13		13	18		18	5		5	10		10	4		4	11		11

	CASE D: Source Wells With Low Concentrations (Concentrations < Median Concentrations from Source Well Database)

	\multicolumn{3}{c}{PCE}	\multicolumn{3}{c}{TCE}	\multicolumn{3}{c}{cis-DCE}	\multicolumn{3}{c}{VC}	\multicolumn{3}{c}{12-DCA}	\multicolumn{3}{c}{111-TCA}
	k$_s$ l/yr	Source Trend	t$_{1/2}$ yr	k$_s$ l/yr	Source Trend	t$_{1/2}$ yr	k$_s$ l/yr	Source Trend	t$_{1/2}$ yr	k$_s$ l/yr	Source Trend	t$_{1/2}$ yr	k$_s$ l/yr	Source Trend	t$_{1/2}$ yr	k$_s$ l/yr	Source Trend	t$_{1/2}$ yr
Maximum	-3.93	Expanding	NA	-1.43	Expanding	NA	-0.02	Expanding	NA	-0.32	Expanding	NA	-3.93	Expanding	NA	-0.34	Expanding	NA
90 Percentile	-0.81	Expanding	NA	-0.86	Expanding	NA	0.14	Shrinking	5.04	-0.12	Expanding	NA	-0.94	Expanding	NA	-0.13	Expanding	NA
75 Percentile	-0.25	Expanding	NA	-0.45	Expanding	NA	0.30	Shrinking	2.29	0.04	Shrinking	16.77	-0.02	Expanding	NA	-0.09	Expanding	NA
50 Percentile	**-0.03**	**Expanding**	**NA**	**-0.04**	**Expanding**	**NA**	**0.47**	**Shrinking**	**1.48**	**0.13**	**Shrinking**	**5.51**	**0.06**	**Shrinking**	**10.78**	**0.04**	**Shrinking**	**16.68**
25 Percentile	0.23	Shrinking	3.06	0.30	Shrinking	2.30	0.68	Shrinking	1.03	0.37	Shrinking	1.86	0.51	Shrinking	1.37	0.17	Shrinking	3.99
10 Percentile	0.47	Shrinking	1.46	0.72	Shrinking	0.96	0.73	Shrinking	0.95	0.63	Shrinking	1.09	0.68	Shrinking	1.03	0.30	Shrinking	2.29
Minimum	1.84	Shrinking	0.38	0.93	Shrinking	0.74	0.76	Shrinking	0.91	0.90	Shrinking	0.77	1.25	Shrinking	0.55	1.50	Shrinking	0.46
Median r^2	0.30			0.45			0.46			0.23			0.71			0.07		
Median conc (mg/L)	0.05			0.35			2.16			0.03			0.05			0.03		
Total no. of sites	19		19	19		19	6		6	8		8	9		9	12		12

NOTE: The Source Decay Rate Constant (k$_s$) is used in a first-order decay relationship to describe how quickly the dissolved concentrations in the source zone (i.e., concentrations that are directly controlled by the rate of NAPL dissolution and/or the rate of desorption from the aquifer material) decline over time. This rate constant is not the same rate constant that represents the attenuation of dissolved-phase constituents that have left the source zone (k) or the biodegradation of dissolved constituents ( ). See Appendix A.1 for more information. NA = Not Applicable.
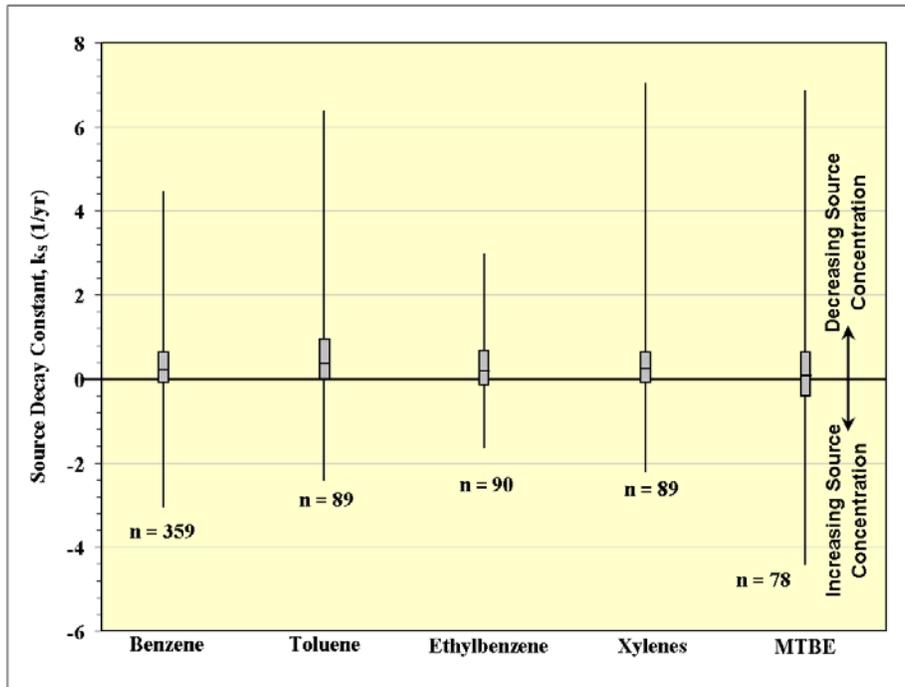
FIGURE 7. Source decay constants for petroleum hydrocarbon sites for Case B, source wells only. Source decay constant derived from linear regression of at least 3 years of concentration versus time data from highest concentration wells at each site. Source half-life = $0.693/k_s$
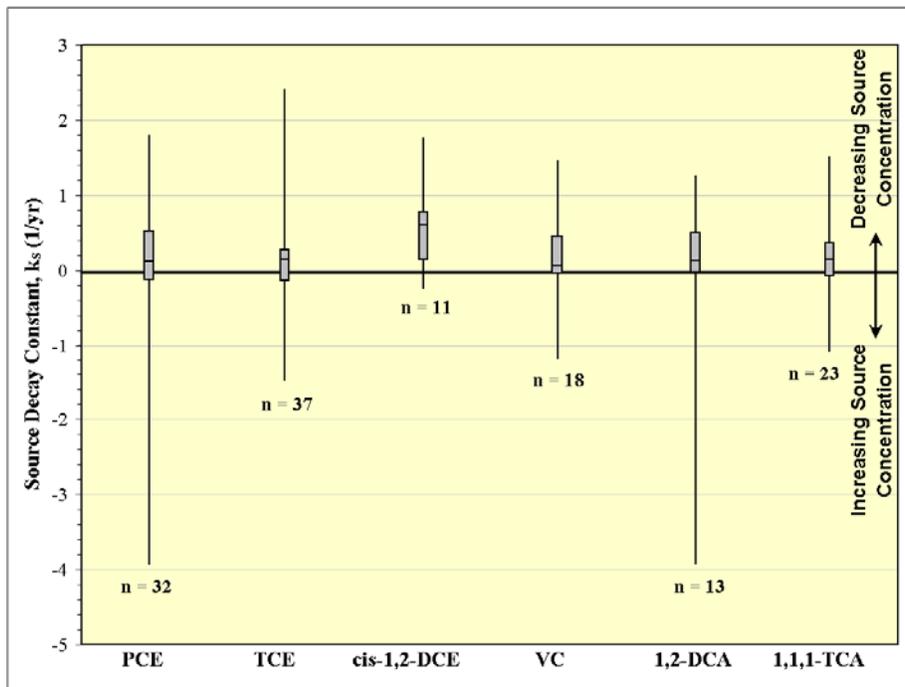
FIGURE 8. Source decay constants for chlorinated solvent sites for Case B, source wells only. Source decay constant derived from linear regression of at least 3 years of concentration versus time data from highest concentration wells at each site. Source half-life = $0.693/k_s$

"Exit Criteria" Used to Close Sites

Risk-Based Decision-making (RBD) is increasingly used by regulators and industry to facilitate corrective action at petroleum release sites. RBD provides a tiered approach for evaluating sites on the basis of potential human health and ecological risk. For advanced tier analyses, extensive and potentially costly site-specific data often must be collected and incorporated into RBD calculations and/or models. Yet in many cases, extensive collection of site-specific data is not needed to make a determination to eliminate a site from further RBCA analysis. At sites for which all receptors are at significant distances from the source, or at sites for which subsurface conditions significantly attenuate chemical transport, concentrations at the receptor might be so low as to not be expected to be above target levels. Such determinations could be made with relatively little site-specific data, and these sites potentially eliminated from consideration for more detailed, and more costly, RBD analyses.

Exit criteria are RBD points at which a determination can be made from limited, readily collected site-specific data that all receptors are at sufficient distances from the source, and/or site subsurface conditions sufficiently attenuate chemical transport, that concentrations at all receptor locations would be so low as to not be expected to be above target levels. Examples of currently existing exit criteria throughout the nation are shown on Figure 9. These exit criteria vary from water depths below ground surface in California to proximity of water supply wells or distribution systems in Massachusetts.
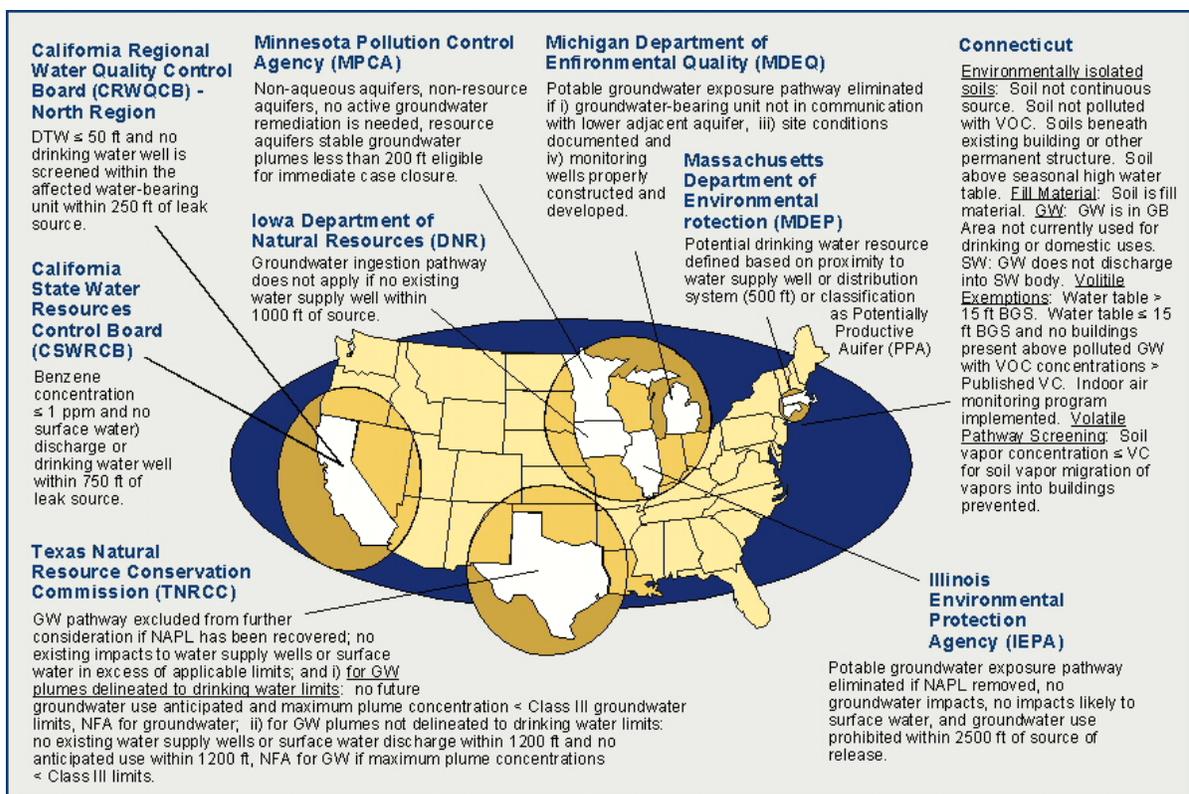
FIGURE 9. Examples of Currently Existing Exit Criteria for Petroleum Hydrocarbon Sites

GLOSSARY OF TERMS

Parameter	Definition	Typical Value
Tier 1 Terms		
k_s	Source decay rate constant. Used in a first-order decay relationship to describe how quickly the dissolved concentrations in the source zone decline over time.	See Chemical Parameter Database, page 65.
Concentration	Concentration measurements of dissolved organics in wells near the centerline of the plume obtained after time = 0..	0.0001 - 500 mg/L
Tier 2 Terms		
V_d	Groundwater Darcy velocity through the "box" (the source zone).	0.2 - 200 ft/yr
K	Hydraulic conductivity. Measure of the permeability of the saturated porous medium.	See Geologic Parameter Database, page 67.
i	Hydraulic gradient. The slope of the potentiometric surface.	0.001 - 0.1 ft/ft
C_{gwo}	Source groundwater concentration. Aqueous phase concentration of constituents in the source zone at time = 0.	0.001 - 500 mg/L
S_l	Source length. Estimated length of the box model of the source zone parallel to groundwater flow.	10 - 500 ft
S_w	Source width. The estimated width of the box model of the source zone perpendicular to groundwater flow.	0 - 500 ft
S_t	Source thickness. The estimated saturated thickness of the box model of the source zone.	5 - 50 ft
Q	Specific discharge. Groundwater flowing through source zone.	100 - 10^6 ft^3/yr
k_s	Source decay rate constant. Used in a first-order decay relationship to describe how quickly the dissolved concentrations in the source zone decline over time.	See Chemical Parameter Database, page 65.
M_o	Source mass. The amount of the constituent of interest that is contained in different "compartments" in the source zone	0.1 - 100,000 kg
Soil Bulk Density	Density of the dry aquifer material.	See Geologic Parameter Database, page 67.
Saturated Zone Total Porosity	Dimensionless ratio of the volume of voids to the bulk volume of the surface soil column matrix.	See Geologic Parameter Database, page 67.
Saturated Zone Soil Density	Density of the saturated aquifer material including soil moisture.	2.0 - 2.2 g/cm^3

Parameter	Definition	Typical Value
Tier 2 Terms Cont'd		
Retardation Factor	Ratio of the dissolved plus sorbed constituent mass to the dissolved constituent mass in the aqueous phase in a unit volume of aquifer.	1 - 3 (typical for BTEX) 2 - 5 (typical for chlorinated solvents)
Affected Area	Area of the affected layer for the compartment of interest for the arithmetic and geometric mean averaging methods.	100 - 500,000 ft^2
Soil Concentration	Multiple soil phase concentration of constituents in the saturated NAPL source zone compartment at time = 0 for the layer of interest.	0.01 - 1,000 mg/kg
Groundwater Concentration	Multiple dissolved concentration of constituents in dissolved compartment at time = 0 for the layer of interest.	0.01 - 1,000 mg/L
Layer Length	Length of the affected layer for the compartment of interest.	10 - 2,000 ft
Layer Width	Width of the affected layer for the compartment of interest.	10 - 1,000 ft
Layer Thickness	Thickness of the affected layer for the compartment and layer of interest.	5 - 50 ft
Area	Area of the affected sample for the compartment of interest.	100 - 500,000 ft^2
Layer Shape	Shape of the affected layer.	-
NAPL Saturation	An estimate of the fraction of pore space filled with NAPL.	0 - 0.30
Constituent Mass Fraction	Chemical and mixture-specific value expressing how much of a mixture consists of one particular constituent, on a mass basis, such as how much of a gasoline sample consists of benzene.	0.12 - 3.5% (Benzene) 0.36 - 2.86% (Ethylbenzene) 2.73 - 21.8% (Toluene) 3.22 - 8.31% (Xylene)
Density of Source NAPL	Density of source NAPL.	0.8 - 1.4 g/cm^3
Lambda (λ)	Biodegradation rate constant of dissolved constituents in groundwater.	0.07 - 43 yr^{-1}
BC	Biodegradation capacity. An estimate of the amount of biodegradation that upgradient groundwater can support.	7 - 70 mg/L
DO	Delta oxygen. This parameter, used in the biodegradation model, is one component of the total biodegradation capacity of the groundwater as it flows through the source zone and constituent plume.	0.4 - 12.7 mg/L
N0$_3$	Delta nitrate. This parameter, used in the biodegradation model, is one component of the total biodegradation capacity of the groundwater as it flows through the source zone and constituent plume.	0 - 69.7 mg/L

Parameter	Definition	Typical Value
Tier 2 Terms Cont'd		
Fe^{2+}	Observed ferrous iron. This parameter is one component of the total biodegradation capacity of the groundwater as it flows through the source zone and constituent plume.	0 - 599.5 mg/L
SO_4	Delta sulfate. This parameter is one component of the total biodegradation capacity of the groundwater as it flows through the source zone and constituent plume.	0 - 109.2 mg/L
CH_4	Observed Methane. This parameter is one component of the total biodegradation capacity of the groundwater as it flows through the source zone and constituent plume.	0 - 48.4 mg/L
Percentage of Biodegradation Capacity	Amount the total biodegradation capacity must be reduced to account for electron acceptor utilization by other dissolved constituents present in the plume.	0 - 100%
Uncertainty Rage for Mass Estimate	An estimate of the uncertainty associated with the source mass estimate for the constituent being modeled.	2 - 100
Tier 3 Terms		
C_o	Original constituent concentration. Average concentration of dissolved constituents in wells within the control volume (the area of interest) at time = 0.	0.01 - 500 mg/L
C_t	Desired cleanup level for the constituent.	-
L	Length of source zone parallel to groundwater flow. Length of plume along flow path in control volume (the portion of the plume of interest) parallel to the groundwater flow.	10 - 1,000 ft
V_s	Groundwater seepage velocity (as applied in Method 1). Actual interstitial groundwater velocity, equaling Darcy velocity divided by effective porosity.	1 - 1,500 ft/yr
R	Ratio of the dissolved plus sorbed constituent mass to the dissolved constituent mass in the aqueous phase in a unit volume of aquifer.	1 - 3 (typical for BTEX) 2 - 5 (typical for chlorinated solvents)
Rho	Soil bulk density (as applied in Method 1). Density of the saturated aquifer material, excluding soil moisture.	See Geologic Parameter Database , page 67.
K_{oc}	Partition coefficient. Chemical-specific partition coefficient between soil organic carbon and the aqueous phase.	See Chemical Parameter Database , page 65.

Parameter	Definition	Typical Value
Tier 3 Terms Cont'd		
f_{oc}	Fraction organic carbon. Fraction of the aquifer material comprised of natural organic carbon in uncontaminated areas.	0.0002 - 0.02
n_e	Effective porosity. Dimensionless ratio of the volume of interconnected voids to the bulk volume of the aquifer matrix.	See Geologic Parameter Database , page 67.
Type of Media	A general description of how well sorted the aquifer material is.	-
C_s	Initial aqueous-phase concentration in source zone. Average concentration of dissolved constituents in wells within the control volume (the area of interest) at time = 0.	0.01 - 500 mg/L
Rho	Density of the source NAPL (as applied in Method 2).	0.8 - 1.4 g/cm^3
S_o	Initial NAPL saturation in porous media. An estimate of the fraction of the pore space filled with NAPL.	0 - 0.30
V_s	Natural groundwater seepage velocity (as applied in Method 2). Actual interstitial groundwater velocity, equaling Darcy velocity divided by effective porosity for natural condition in aquifer.	1 - 1,500 ft/yr
L	Length of source zone parallel to groundwater flow. Length of plume along flow path in control volume parallel to the groundwater flow.	10 - 1,000 ft
Typical Groundwater Seepage Velocity While Pumping	Average groundwater seepage velocity in control volume while pumping.	1 - 3,000 ft/yr
Concentration in Produced Groundwater	Initial aqueous-phase concentration while pumping, as impacted by mass transfer effects, prior to flushing.	0.01 - 50 mg/L
PV	Number of pore volumes. A pore volume is the volume of water required to replace water in a unit volume of saturated porous media.	-
Time to Flush Out Constituents	Time required to flush out the constituents from the source zone, after accounting for the presence of NAPL.	-

CHEMICAL PARAMETER DATABASE

Chemical Name	Organic Carbon Petitioning Coefficient (log (Koc) @20-25 C)) (log (1/kg))*	Solubility (@20-25 C) (mg/L)*	Source Decay Rate (k_s) (1/yr)**
Acetone	-0.24	1.00×10^6	
Acenaphthene	3.85	3.93×10^0	
Acenaphthylene	4.00	3.93×10^0	
Anthracene	4.15	4.50×10^{-2}	
Benzene	1.58	1.75×10^3	0.16-0.30
Benzoic acid	1.83	6.22×10^4	
Benzo (a) Anthracene	6.14	5.70×10^{-3}	
Benzo (b) Fluoranthane	5.74	1.47×10^{-2}	
Benzo (k) Fluoranthene	5.74	4.30×10^{-3}	
Benzo (g,h,i) Perylene	6.20	7.00×10^{-4}	
Benzo (a) Pyrene	5.59	1.20×10^{-3}	
Bromodichloromethane	1.85	6.22×10^1	
Butanol, n-	0.74	7.70×10^4	
Carbon disulfide	2.47	2.30×10^3	
Carbon tetrachloride	2.67	7.62×10^2	
Chlorobenzene	2.46	4.45×10^2	
Chloroethane	1.25	2.00×10^4	
Chloroform	1.93	9.64×10^3	
Chloromethane	1.40	4.00×10^{-3}	
Chlorophenol, 2-	2.11	2.85×10^4	
Chrysene	5.30	1.80×10^{-3}	
Dibenzo (a,h) Anthracene	5.87	5.00×10^{-4}	
Dibromochloromethane	2.05	5.25×10^3	
Dichlorobenzene, (1,2) (-o)	3.32	1.50×10^2	
Dichlorobenzene, (1,4) (-p)	3.33	1.45×10^2	
Dichlorodifluoromethane	2.12	1.98×10^3	
Dichloroethane, 1,1-	1.76	5.00×10^3	
Dichloroethane, 1,2-	1.76	8.69×10^3	0.02-0.30
Dichloroethene, cis1,2-	1.38	8.00×10^2	0.11-0.81
Dichloroethene, trans1,2-	1.46	1.75×10^3	
Ethylbenzene	1.98	6.00×10^2	0.16-0.22
Ethylene glycol	-0.90	1.00×10^6	
Fluoranthene	4.58	2.06×10^{-1}	
Fluorene	3.86	1.69×10^0	
Hexane, n-	2.68	1.30×10^1	
Indeno (1,2,3,c,d) Pyrene	7.53	7.17×10^2	
Methanol	-0.69	1.00×10^6	
Methylene chloride	1.23	1.54×10^4	
Methyl ethyl ketone	0.28	2.18×10^5	

Chemical Name	Organic Carbon Petitioning Coefficient (log (Koc) @20-25 C)) (log (1/kg))*	Solubility (@20-25 C) (mg/L)*	Source Decay Rate (k_s) (1/yr)**
Methyl t-Butyl Ether	1.08	4.80×10^4	0.15-0.31
Naphthalene	3.11	3.29×10^1	
Phenanthrene	4.15	1.60×10^0	
Phenol	1.44	9.30×10^4	
Pyrene	4.58	1.60×10^{-1}	
Tetrachloroethane 1,1,2,2-	0.00	7.18×10^2	
Tetrachloroethene	2.43	1.43×10^2	0.03-0.50
Toluene	2.13	5.15×10^2	0.38-0.44
Trichlorobenzene	3.91	3.03×10^1	
Trichloroethane 1,1,1-	2.45	1.26×10^3	0.04-0.31
Trichloroethane 1,1,2-	1.75	5.93×10^3	
Trichloroethene	1.26	1.00×10^3	0.04-0.18
Trichlorofluoromethane	2.49	2.47×10^3	
Vinyl Chloride	0.39	2.54×10^3	0.07-0.13
Xylene (mixed isomers)	2.38	1.98×10^2	0.19-0.25
Xylene, m-	3.20	1.58×10^2	
Xylene, o-	2.11	1.75×10^2	

* Values obtained from "Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface" by Wiedemeier *et al*., 1999, Appendix B.

** See "Background Information for SourceDK Modeling", page 53.

GEOLOGIC PARAMETER DATABASE

Parameter	Value	Units
Hydraulic Conductivity[1]		
Clean sands	1×10^{-3}-1	cm/s
Clays	$<1 \times 10^{-6}$	cm/s
Gravels	>1	cm/s
Silts	1×10^{-6}-1×10^{-3}	cm/s
Silty sands	1×10^{-5}-1×10^{-1}	cm/s
Total Porosity[2]		
Basalt	0.03-0.35	(-)
Clay	0.34-0.60	(-)
Coarse Gravel	0.24-0.36	(-)
Fine Gravel	0.25-0.38	(-)
Fine Sand	0.26-0.53	(-)
Coarse Sand	0.31-0.46	(-)
Limestone	0.0-0.5	(-)
Sandstone	0.05-0.30	(-)
Shale	0.0-0.10	(-)
Silt	0.34-0.61	(-)
Siltstone	0.21-0.41	(-)
Effective Porosity[3]		
Clay	0.01-0.20	(-)
Fine Gravel	0.2-0.35	(-)
Medium Gravel	0.15-0.25	(-)
Coarse Gravel	0.1-0.25	(-)
Sandy Clay	0.03-0.2	(-)
Loess	0.15-0.35	(-)
Peat	0.3-0.5	(-)
Silt	0.01-0.3	(-)
Gravely Sand	0.2-0.35	(-)
Fine Sand	0.10-0.30	(-)
Medium Sand	0.15-0.30	(-)
Coarse Sand	0.20-0.35	(-)
Glacial Sediments	0.05-0.2	(-)
Limestone	0.01-0.24	(-)
Unfractured Limestone	0.001-0.05	(-)
Sandstone	0.1-0.4	(-)
Siltstone	0.01-0.35	(-)
Fractured Granite	0.00005-0.01	(-)
Volcanic Tuff	0.02-0.35	(-)
Dry Bulk Density[2]		
Clay	1.00-2.40	(g/cm^3)
Silt	-	(g/cm^3)

Parameter	Value	Units
Granite	2.24-2.46	(g/cm^3)
Fine Sand	1.37-1.81	(g/cm^3)
Medium Sand	1.37-1.81	(g/cm^3)
Coarse Sand	1.37-1.81	(g/cm^3)
Sandstone	1.60-2.68	(g/cm^3)
Gravel	1.36-2.19	(g/cm^3)
Limestone	1.74-2.79	(g/cm^3)

Notes:

1. From Newell *et al*., 1996.
2. From Wiedemeier *et al*., 1995.
3. From Wiedemeier *et al*., 1999 (originally from Domenico and Schwartz, 1990 and Walton, 1998).

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SourceDK TROUBLESHOOTING TIPS

Minimum System Requirements

The SourceDK model requires a computer system capable of running Microsoft© Excel (97-SR1/ 2000/XP) for Windows (98/2000/XP). Operation requires an IBM-compatible PC equipped with a Pentium or later processor running at a minimum of 450 MHz. A minimum of 256 MB of system memory (RAM) is strongly recommended. Computers not meeting these recommendations will experience slow running times and/or problems with memory.

Installation and Start-Up

The software is installed by copying the SourceDK model file (SourceDK.xls) and the SourceDK help file (SourceDK.hlp) to the same folder on your computer hard drive. To use the software, start Excel and load the SourceDK model file from the File / Open menu. If you are using Excel 2000, you may see a message box that asks you whether you want to disable or enable the macros. For SourceDK to operate effectively, you must *enable* the macros.

Spreadsheet-Related Problems

Backspace doesn't clear cell in Tier 1. Use the delete key on the keyboard or the mouse to clear data in Tier 1.

Can't see all three lines (mid, high, and low range estimates) in Tier 2 output. Sometimes one or more of the lines may overlap because of rapidly declining mass. Additionally, the minimum value plotted in the logarithmic scale is 0.001 mg/L. To view the decays, decrease the Number of Years Over Which to Plot Data considerably.

The buttons won't work. SourceDK is built in the Excel spreadsheet environment, and to enter data one must click anywhere outside the cell where data was just entered. If you can see the numbers you just entered in the data entry part of Excel above the spreadsheet, the data have not yet been entered. Click on another cell to enter the data.

is displayed in a number box. The cell format is not compatible with the value, (e.g., the number is too big to fit into the window). To fix this, unprotect the sheet. Then, select the cell, pull down the format menu, select *Cells* and click on the *Number* tab. Change the format of the cell until the value is visible. If the values still cannot be read, select the format menu, select *Cells* and click on the *Font* tab. Reduce the font size until the value can be read.

#DIV/0! is displayed in a number box. The most common cause of this problem is that some input data are missing. In some cases, entering a zero in a box will cause this problem. Double check to make certain that data required for your run have been entered in all of the input cells.

#VALUE! is displayed in a number box. The most common cause of this problem is that some input data are missing. Double check to make certain that data required for your run have been entered in all of the input cells and all options have been selected.

The source dialog boxes keep closing. If you press *Enter* when inputting data in a dialog box (pop-up window) then the dialog box will close. Do not press *Enter* to move to the next cell. Use tab key or the mouse to move to the next cell. If you do press *Enter* by accident, simply select your source option again.

The time in the Output Screen is not in sequential order. You have not entered the field data time in ascending order in the Input screen. Make sure you don't have any blank cells in the time cells.

Common Error Messages

Unable to Load Help File: The most common error message encountered with SourceDK is the message 'Unable to Open Help File' after clicking on a *Help* button. Depending on the version of Windows you are using, you may get an Excel Dialog Box, a Windows Dialog Box, or you may see Windows Help load and display the error. This problem is related to the ease with which the Windows Help Engine can find the data file, SourceDK.HLP. Here are some suggestions (in decreasing order of preference) for helping WinHelp find it:

- • If you are asked to find the requested file, do so. The file is called SourceDK.HLP, and it was installed in the same directory/folder as the SourceDK model file (SourceDK.xls).

- • Use the File/Open menus from within Excel instead of double-clicking on the filename or Program Manager icon to open the SourceDK model file. This sets the *current directory* to the directory containing the Excel file you just opened.

ACKNOWLEDGEMENTS

SourceDK Review Team:	Ms. Robin Davis Utah Department of Environmental Quality 150 North 1850 West Salt Lake City, Utah 84116
SourceDK Review Team:	Ms. AnnMarie Spexet Ms. Dana Rowan Mr. Adam Luke Groundwater Services, Inc. 2211 Norfolk, Ste. 1000 Houston, Texas 77098

APPENDICES

APPENDIX A.1.   APPROPRIATE USE OF FIRST ORDER RATE CONSTANTS FOR MONITORED NATURAL ATTENUATION STUDIES

Ground Water Issue

Calculation and Use of First-Order Rate Constants for Monitored Natural Attenuation Studies

Charles J. Newell[1], Hanadi S. Rifai[2], John T. Wilson[3], John A. Connor[1], Julia A. Aziz[1], and Monica P. Suarez[2]

Introduction

This issue paper explains when and how to apply first-order attenuation rate constant calculations in monitored natural attenuation (MNA) studies. First-order attenuation rate constant calculations can be an important tool for evaluating natural attenuation processes at ground-water contamination sites. Specific applications identified in U.S. EPA guidelines (U.S. EPA, 1999) include use in characterization of plume trends (shrinking, expanding, or showing relatively little change), as well as estimation of the time required for achieving remediation goals. However, the use of the attenuation rate data for these purposes is complicated as different types of first-order rate constants represent very different attenuation processes:

Concentration vs. time rate constants (k_{point}) are used for estimating how quickly remediation goals will be met at a site.

Concentration vs. distance bulk attenuation rate constants (k) are used for estimating if a plume is expanding, showing relatively little change, or shrinking due to the combined effects of dispersion, biodegradation, and other attenuation processes.

Biodegradation rate constants (λ) are used in solute transport models to characterize the effect of biodegradation on contaminant migration.

Correct use of attenuation rate constants requires an understanding of the different attenuation processes that different first-order rate constants represent.

For further information contact John T. Wilson (580) 436-8534 at the Subsurface Protection and Remediation Division of the National Risk Management Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Ada, Oklahoma.

Why Are Attenuation Rate Constants Important?

Monitored natural attenuation (MNA) refers to the reliance on natural attenuation processes to achieve site-specific remediation objectives within a reasonable time frame. Natural attenuation processes include a variety of physical, chemical, and/or biological processes that act without human intervention to reduce the mass

or concentration of contaminants in soil and ground water. These in-situ processes include biodegradation, dispersion, dilution, sorption, volatilization; radioactive decay; and chemical or biological stabilization, transformation, or destruction of contaminants (U.S. EPA, 1999).

The overall impact of natural attenuation processes at a given site can be assessed by evaluating the rate at which contaminant concentrations are decreasing either spatially or temporally. Recent guidelines issued by the U.S. EPA (U.S. EPA, 1999) and the American Society for Testing and Materials (ASTM, 1998) have endorsed the use of site-specific attenuation rate constants for evaluating natural attenuation processes in ground water. The U.S. EPA directive on the use of Monitored Natural Attenuation (MNA) at Superfund, RCRA, and UST sites (U.S. EPA, 1999) includes several references to the application of attenuation rates:

Once site characterization data have been collected and a conceptual model developed, the next step is to evaluate the potential efficacy of MNA as a remedial alternative. This involves collection of site-specific data sufficient to estimate with an acceptable level of confidence both the rate of attenuation processes and the anticipated time required to achieve remediation objectives.

At a minimum, the monitoring program should be sufficient to enable a determination of the rate(s) of attenuation and how that rate is changing with time.

Site characterization (and monitoring) data are typically used for estimating attenuation rates.

The ASTM Standard Guide for Remediation of Groundwater by Natural Attenuation at Petroleum Release Sites (ASTM, 1998) also identifies site-specific attenuation rates as a secondary line of evidence of the occurrence and rate of natural attenuation. In addition, technical guidelines issued by various state environmental regulatory agencies recommend estimation of rate constants to evaluate contaminant plume trends and duration (New Jersey DEP, 1998; Wisconsin DNR, 1999). For example, the New Jersey Department of Environmental Protection (DEP) now requires such calculations for establishing "Classification Exception Areas (CEAs)" at sites where ground-water quality standards are or will be exceeded for an extended time period.

The technical literature contains numerous guidelines regarding methods for derivation of site-specific attenuation rate constants based upon observed plume concentration trends (e.g., ASTM, 1998; U.S. EPA, 1998a; 1998b; Wiedemeier et al. 1995; 1999; Wilson and Kolhatkar, 2002). Other resources, such as the

[1]Groundwater Services, Inc., Houston, Texas

[2]University of Houston, Texas

[3]U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Subsurface Protection and Remediation Division, Ada, Oklahoma

BIOSCREEN and BIOCHLOR natural attenuation models (Newell et al., 1996; Aziz et al., 2000), include use of first-order rate constants for simulating the attenuation of dissolved contaminants once they leave the source and the attenuation of the source itself. However, many of these references do not clearly distinguish between the different types of rate constants and their appropriate application in evaluation of natural attenuation processes. The objective of this paper is to address this gap by briefly describing the derivation, significance, and appropriate use of three key types of attenuation rate constants commonly employed in natural attenuation studies.

Key Point:

Rate calculations can help those performing MNA studies evaluate the contribution of attenuation processes and the anticipated time required to achieve remediation objectives. There are different types of rate calculations, however, and it is important to use the right kind of rate constant for the right application.

Types of First-Order Attenuation Rate Constants

In general, there are three different types of first-order attenuation rate constants that are in common use:

Concentration vs. Time Attenuation Rate Constant, where a rate constant, in units of inverse time (e.g., per day), is derived as the slope of the natural log concentration vs. time curve measured at a selected monitoring location (Figure 1).
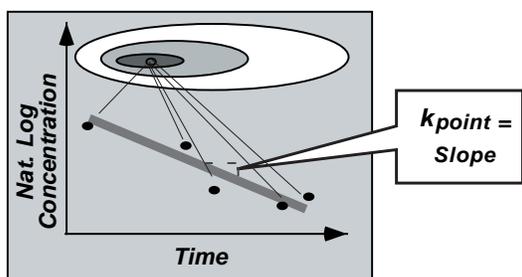
Figure 1. Determining concentration vs. time rate constant (k_{point}).

Concentration vs. Distance Attenuation Rate Constant, where a rate constant, in units of inverse time (e.g., per day), is derived by plotting the natural log of the concentration vs. distance and (if determined to match a first-order pattern) calculating the rate as the product of the slope of the transformed data plot and the ground-water seepage velocity (Figure 2).
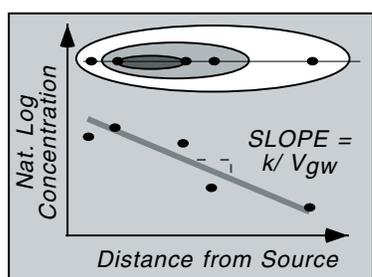
Figure 2. Determining concentration vs. distance rate constant (k).

Biodegradation Rate Constant. The "biodegradation rate constant" (λ) in units of inverse time (e.g., per day) can be derived by a variety of methods, such as comparison of

contaminant transport vs. transport of a tracer, or more commonly, calibration of solute transport model to field data (Figure 3).
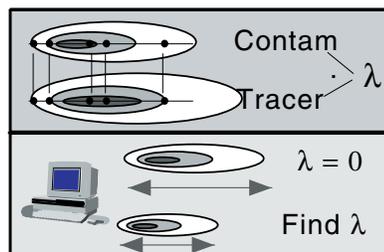
Figure 3. Determining biodegradation rate constant (λ).

Distinctions Between Rate Constants

To interpret the past behavior of plumes, and to forecast their future behavior, it is necessary to describe the behavior of the plume in both space and time. It is necessary to collect long-term monitoring data from wells that are distributed throughout the plume. *Concentration vs. Time Rate Constants* describe the behavior of the plume at one point in space; while *Concentration vs. Distance Rate Constants* describe the behavior of the entire plume at one point in time. The *Biodegradation Rate Constant* is usually applied over both time and space, but only applies to one attenuation mechanism. Standard practice for the environmental industry finds applications for each of these rate constants. Under appropriate conditions, each of the three constants can be employed to assist in site-specific evaluation and quantification of natural attenuation processes. Each of these terms is identified as an "attenuation rate." Because they differ in their significance and appropriate application, it is important to understand the potential for misapplication of each type of rate as summarized below:

Concentration vs. Time Rate Constants: A rate constant derived from a concentration vs. time (C vs. T) plot at a single monitoring location provides information regarding the potential plume lifetime at that location, but cannot be used to evaluate the distribution of contaminant mass within the ground-water system. The C vs. T rate constant at a location within the source zone represents the persistence in source strength over time and can be used to estimate the time required to reach a remediation goal at that particular location. To adequately assess an entire plume, monitoring wells must be available that adequately delineate the entire plume, and an adequate record of monitoring data must be available to calculate a C vs. T plot for each well. At most sites, the rate of attenuation in the source area (due to weathering of residual source materials such as NAPLs) is slower than the rate of attenuation of materials in ground water, and concentration profiles in plumes tend to retreat back toward the source over time. In this circumstance, the lifecycle of the plume is controlled by the rate of attenuation of the source, and can be predicted by the C vs. T plots in the most contaminated wells. At some sites, the rate of attenuation of the source is rapid compared to the rate of attenuation in ground water. This pattern is most common when contaminants are readily soluble in ground water and when contaminants are not biodegraded in ground water. In this case, the rate of attenuation of the source as predicted by a C vs. T plot will underestimate the lifetime of the plume.

Concentration vs. Distance Rate Constants: Attenuation rate constants derived from concentration vs. distance (C vs. D)

plots serve to characterize the distribution of contaminant mass within *space* at a given point in time. A single C vs. D plot provides no information with regard to the variation of dissolved contaminant mass over *time* and, therefore, cannot be employed to estimate the time required for the dissolved plume concentrations to be reduced to a specified remediation goal. This rate constant incorporates all attenuation parameters (sorption, dispersion, biodegradation) for dissolved constituents after they leave the source. Use of the rate constant derived from a C vs. D plot (i.e., characterization of contaminant mass over space) for this purpose (i.e., to characterize contaminant mass over time) will provide erroneous results. The C vs. D-based rate constant indicates how quickly dissolved contaminants are attenuated once they leave the source but provides no information on how quickly a residual source zone is being attenuated. Note that most sites with organic contamination will have some type of continuing residual source zone, even after active remediation (Wiedemeier et al., 1999), making the C vs. D rate constant inappropriate for estimating plume lifetimes for most sites.

Biodegradation Rate Constant: Another type of error occurs if a C vs. D rate constant is used as the biodegradation rate term (λ) in a solute transport model. The attenuation rate constant derived from the C vs. D plot already reflects the combined effects of contaminant sorption, dispersion, and biodegradation. Consequently, use of a C vs. D rate constant as the biodegradation rate within a model that separately accounts for sorption and dispersion effects will significantly overestimate attenuation effects during ground-water flow.

These examples serve to illustrate the need to ensure an appropriate match between the significance and use of each rate constant. Further guidelines regarding derivation and use of attenuation rate constants are provided below.

Key Point:

There are three general types of first-order rate constants that are commonly used for MNA studies: (1) Concentration vs. Time, (2) Concentration vs. Distance, and (3) Biodegradation.

Rate Constants vs. Half-Lives

Both first-order rate constants and attenuation half-lives represent the same process, first-order decay. Some environmental professionals prefer to use rate constants (in units of per time) to describe the first-order decay process, while others prefer half-lives. These two terms are linearly related by:

Rate constant = 0.693 / [half-life] and
Half-life = 0.693 / [rate constant]

For example, a 2 year half-life is equivalent to a first-order rate constant of 0.35 per year. This document describes the first-order decay process in terms of rate constants instead of half-lives.

Key Point:

Rate constants and half-lives represent the same first-order decay process, and are inversely related.

Appropriate Use of Attenuation Rate Constants in Natural Attenuation Studies

Attenuation rate constants may be used for the following three purposes in natural attenuation studies:

Plume Attenuation: Demonstrate that contaminants are being attenuated within the ground-water flow system;

Plume Trends: Determine if the affected ground-water plume is expanding, showing relatively little change, or shrinking; and

Plume Duration: Estimate the time required to reach ground-water remediation goals by natural attenuation alone.

Appropriate use of the various attenuation rate constants for evaluation of plume attenuation, trends, and duration is shown in Table 1.

As described in the U.S. EPA MNA Directive (U.S. EPA, 1999):

Site characterization (and monitoring) data are typically used for estimating attenuation rates. These calculated rates may be expressed with respect to either time or distance from the source. Time-based estimates are used to predict the time required for MNA to achieve remediation objectives and distance-based estimates provide an evaluation of whether a plume will expand, remain stable, or shrink.

To clarify the applicability of the various first-order decay rate constants, appropriate nomenclature is useful to indicate the significance of each term. For example, **point decay rates** (defined

Table 1. Summary of First-Order Rate Constants for Natural Attenuation Studies

Rate Constant	Method of Analysis	Significance	Use of Rate Constant		
			Plume Attenuation	Plume Trends?	Plume Duration?
Point Attenuation Rate (Fig. 1) (k_{point}, time per year)	C vs. T Plot	Reduction in contaminant concentration over time at a single point	NO*	NO*	YES
Bulk Attenuation Rate (Fig. 2) (k; time per year)	C vs. D Plot	Reduction in dissolved contaminant concentration with distance from source	YES	NO*	NO
Biodegradation Rate (Fig. 3) (λ, time per year)	Model Calibration, Tracer Studies, Calculations	Biodegradation rate for dissolved contaminants after leaving source, exclusive of advection, dispersion, etc.	YES	NO	NO

* Note: Although assessment of an attenuation rate constant at a single location does not yield plume attenuation information, or plume trend information, an assessment of general trends of multiple wells over the entire plume is useful to assess overall plume attenuation and plume trends.

as k_{point}), derived from single well concentration vs. time plot, may be used to determine how long a plume will persist (Plume Duration). While concentration vs. time data at a single point in the plume are useful for determining trends at that location (i.e., are concentrations increasing, showing relatively little change, or declining), a rate constant calculated from concentration vs. time data at a single location cannot be used to estimate the trend of an entire plume.

Bulk attenuation rates (defined as k), derived from concentration vs. distance plots, can be used to indicate if a plume is expanding, showing relatively little change, or shrinking (Plume Trends).

Biodegradation rates (λ), modeling parameters which are specific to biodegradation effects and exclusive of dispersion, etc., can be used in appropriate solute transport models to indicate if a plume is expanding, showing relatively little change, or shrinking (Plume Trends).

For each of these first-order decay rate parameters, Table 2 summarizes information on the derivation and appropriate use as well as providing representative values. In summary, different types of first-order attenuation rate calculations are available to help evaluate natural attenuation processes at contaminated ground-water sites. These different types of rate constants represent different types of attenuation processes, therefore, the right type of rate constant should be used for the right purpose.

Examples 1-3 illustrate how the three types of rate constants are calculated and applied.

Key Point:

In general, all three types of rate constants are useful indicators that attenuation is occurring. Concentration vs. time rate constants (k_{point}) can be used to estimate the duration of contamination at a particular location. Concentration vs. time rate constants for wells encompassing the entire plume can be used to identify overall trends and predict the duration of the plume. Concentration vs. distance rate constants (k) and biodegradation rate constants (λ) can be used to project the rate of attenuation of contaminants along the flow path in ground water, and predict the spatial extent of the plume.

Tables 1 and 2 provide more detail on use, calculations, and analysis of the three types of rate constants. Examples 1-3 illustrate the use and application of the three types of rate constants.

Other Types of Rate Constants

Mass-Based Rate Constants. The previous discussion focused on concentration-based rates. It is also possible to calculate mass vs. time rate constants and mass vs. distance rate constants. In practice, these rates would be very similar to the concentration-based rates.

Mass vs. Time Rate Constant. This constant compares changes in the total mass of contaminants in the plume over time. A Thiessen polygon network can be used to weight the concentration data from all the available wells at a site to derive a comprehensive estimate of the mass of contaminants in the plume at any particular round of sampling. Mass vs. time decay rates (in units of inverse time) are estimated by plotting the natural log of total dissolved mass as a function of time and estimating the slope of the line. This rate is similar to the concentration vs. time rate and since it accounts for the entire plume, it is a good indicator of how long a plume will persist. Many plumes change flow direction over time, making it difficult to identify a stable centerline. Estimates based on the entire plume are less subject to errors caused by changes

in flow direction. See Hyman and DuPont, 2001 and DuPont et al.,1998 for discussion and details of the methods.

Mass Flux vs. Distance Rate Constant. A mass vs. distance decay rate (in units of inverse time) can be calculated by plotting the natural log of mass flux through different transects perpendicular to the flow as a function of distance from the source and multiplying the slope of the best-fit line by the seepage velocity. Comparable to the bulk attenuation rate, this type of rate can be used to indicate if a plume is expanding, showing relatively little change, or shrinking. See Einarson and Mackay, 2001 for examples of mass flux calculations. Another method for calculating mass loss rates is described by the Remediation Technologies Development Forum (RTDF, 1997).

Mass Flux-Based Biodegradation Rate Constant. Mass fluxes across plume transects can be further analyzed to determine whether the observed mass loss spatially and temporally can be attributed to biodegradation and/or source decay. For this purpose, the mass flux across the source area is compared to the mass flux through the next downgradient section. Theoretically, mass fluxes at the downgradient transect should mimic the trends observed in the source transect if source decay, sorption, and dispersion were the only mass reduction attenuation mechanisms. If there is additional mass loss, it can only be attributed to biodegradation since the other processes are already accounted for in the mass flux calculation. Once the actual mass loss attributable to biodegradation has been determined, it is plotted as a function of time and a biodegradation rate is estimated using linear regression or a first-order decay model fit to the data. See Borden et al. (1997) and Semprini et al. (1995) for examples of biodegradation rates calculated from mass flux across transects.

Mass-based rate constants are not often used in practice due to the data needs for mass estimates including a dense well network as well as localized gradients, conductivity measurements, and aquifer thickness at monitoring points.

Average-Plume Concentration Rate Constants. Some researchers and practitioners have calculated rate constants for the change in average plume concentration. This rate constant reflects primarily the change in source strength over time.

Effect of Residual NAPL on Point Decay Rate Constant

When a monitoring well is screened across an interval that contains residual NAPL, and when the rate of weathering of the NAPL is slow, the well water may sustain high concentrations of contaminants over long periods of time.

Effect of NA Processes on Rate Constants

Natural attenuation processes include a variety of physical, chemical, or biological processes that act without human intervention to reduce the mass or concentration of contaminants in soil and ground water. These in-situ processes include biodegradation, dispersion, dilution, sorption, volatilization, radioactive decay, and chemical or biological stabilization, transformation, or destruction of contaminants (U.S. EPA, 1999).

Each of these processes influences contaminant concentrations in soil and ground water both spatially and temporally at a site. Contaminant concentrations in ground water are reduced as they travel downgradient from the source. Subject to source degradation, contaminant concentrations will also be reduced with time at any given distance downgradient from the source. These concepts are illustrated in Appendices II and III. The data in Appendix II illustrate the change in contaminant concentrations downgradient from the source at a hypothetical site in response

to the different attenuation processes. It can be clearly seen from Appendix II that contaminant concentrations downgradient from source areas are attenuated due to dispersion, sorption, biodegradation and source decay. The data in Appendix III illustrate the change in contaminant concentrations with time at two points downgradient from the source at the hypothetical site (one point near the source and the other point at the leading edge of the plume). As can be seen from Appendix III, contaminant concentrations near the source will attenuate with time only if source decay is occurring. While source decay is also important for the leading edge of the plume, maximum contaminant concentrations in that zone are significantly attenuated from their source concentration counterparts due to biodegradation, sorption, and dispersion.

Uncertainty in Rate Calculations

Rate calculations can be affected by uncertainty from a number of sources, such as the design of the monitoring network, seasonal variations, uncertainty in sampling methods and lab analyses, and the heterogeneity in most ground-water plumes. Appendix I discusses uncertainty in rate calculations and provides methods for managing this uncertainty.

ORD has developed software (RaCES) to extract rate constants from field data. This software is intended to facilitate an evaluation of the uncertainty associated with the projections made by computer models of the future behavior of plumes of contamination in ground water. The software is available from The Ecosystem Research Division of the National Exposure Research Laboratory in Athens, Georgia (Budge et al., 2003).

Notice

The U.S. Environmental Protection Agency through its Office of Research and Development funded and managed the research described here under Contract No. 68-C-99-256 to Dynamac Corporation. It has been subjected to the Agency's peer and administrative review and has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Quality Assurance Statement

All research projects making conclusions or recommendations based on environmental data and funded by the U.S. Environmental Protection Agency are required to participate in the Agency Quality Assurance Program. This project did not involve the collection or use of environmental data and, as such, did not require a Quality Assurance Project Plan.

Table 2. Quick Reference Summary of Three Types of Attenuation Rate Constants

	Point Decay Rate Constant (k_{point})	Bulk Attenuation Rate Constant (k)	Biodegradation Rate Constant (λ)
USED FOR:	***Plume Duration Estimate.*** Used to estimate time required to meet a remediation goal at a particular point within the plume. If wells in the source zone are used to derive k_{point}, then this rate can be used to estimate the time required to meet remediation goals for the entire site. k_{point} should no*t* be used for representing biodegradation of dissolved constituents in ground-water models (use λ as described in the right hand column).	***Plume Trend Evaluation.*** Can be used to project how far along a flow path a plume will expand. This information can be used to select the sites for monitoring wells and plan long-term monitoring strategies. Note that k should not be used to estimate how long the plume will persist except in the unusual case where the source has been completely removed, as the source will keep replenishing dissolved contaminants in the plume.	***Plume Trend Evaluation.*** Can be used to indicate if a plume is still expanding, or if the plume has reached a dynamic steady state. First calculate λ, then enter λ into a fate and transport model and run the model to match existing data. Then increase the simulation time in the model and see if the plume grows larger than the plume simulated in the previous step. Note that λ should not be used to estimate how long the plume will persist except in the unusual case where the source has been completely removed.
REPRESENTS:	Mostly the change in source strength over time with contributions from other attenuation processes such as dispersion and biodegradation. k_{point} is not a biodegradation rate as it represents how quickly the source is depleting. In the rare case where the source has been completely removed (for a discussion of source zones, see Wiedemeier et al., 1999), k_{point} will approximate k.	Attenuation of dissolved constituents due to all attenuation processes (primarily sorption, dispersion, and biodegradation).	The biodegradation rate of dissolved constituents once they have left the source. It does not account for attenuation due to dispersion or sorption.
HOW TO CALCULATE:	Plot natural log of concentration vs. time for a single monitoring point and calculate k_{point} = slope of the best-fit line (ASTM, 1998). This calculation can be repeated for multiple sampling points and for average plume concentration to indicate spatial trends in k_{point} as well. Note this calculation *does not* account for any changes in attenuation processes, particularly Dual-Equilibrium Desorption (availability) which can reduce the apparent attenuation rate at lower concentrations (e.g., see Kan et al., 1998).	Plot natural log of conc. vs. distance. If the data appear to be first-order, determine the slope of the natural log-transformed data by: 1. Transforming the data by taking natural logs and performing a linear regression on the transformed data, or 2. Plotting the data on a semi-log plot, taking the natural log of the y intercept minus the natural log of the x intercept and dividing by the distance between the two points. Multiply this slope by the contaminant velocity (seepage velocity divided by the retardation factor R) to get k. 	Adjust contaminant concentration by comparison to existing tracer (e.g., chloride, tri-methyl benzenes) and then use method for bulk attenuation rate (see Wiedemeier et al., 1999); or Calibrate a ground-water solute transport computer model that includes dispersion and retardation (e.g., BIOSCREEN, BIOCHLOR, BIOPLUME III, MT3D) by adjusting λ; or Use the method of Buscheck and Alcantar (1995) (plume must be at steady-state to apply this method). Note this method is a hybrid between k and λ as the Buscheck and Alcantar method removes the effects of longitudinal dispersion, but does not remove the effects of transverse dispersion from their λ.
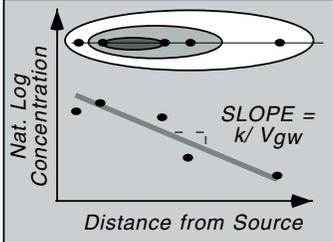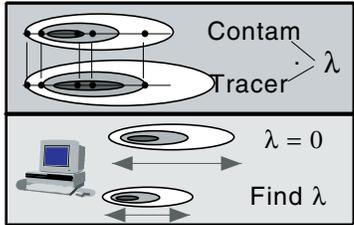
Table 2.   Continued...

	Point Decay Rate Constant (k_{point})	Bulk Attenuation Rate Constant (k)	Biodegradation Rate Constant (λ)
HOW TO USE:	*To estimate plume lifetime:* The time (t) to reach the remediation goal at the point where K_{point} was calculated is: $$t = \frac{-Ln\left[\frac{C_{goal}}{C_{start}}\right]}{k_{point}}$$	*To estimate if a plume is showing relatively little change:* Pick a point in the plume but downgradient of any source zones. Estimate the time needed to decay these dissolved contaminants to meet a remediation goal as these contaminants move downgradient: $$t = \frac{-Ln\left[\frac{C_{goal}}{C_{start}}\right]}{k}$$ Calculate the distance L that the dissolved constituents will travel as they are decaying using V_s as the seepage velocity and R is the retardation factor for the contaminant: $$L = \frac{V_s}{R} \cdot t$$ If the plume currently has not traveled this distance L then this rate analysis suggests the plume may expand to that point. If the plume has extended beyond point L, then this rate analysis suggests the plume may shrink in the future. Note that an alternative (and probably easier method) is to merely extrapolate the regression line to determine the distance where the regression line reaches the remediation goal.	*To estimate if a plume is showing relatively little change:* Enter λ in a solute transport model that is calibrated to existing plume conditions. Increase the simulation time (e.g. by 100 years, or perhaps to the year 2525), and determine if the model shows that the plume is expanding, showing relatively little change, or shrinking.
TYPICAL VALUES:	Reid and Reisinger (1999) indicated that the mean point decay rate constant for benzene from 49 gas station sites was 0.46 per year (half-life of 1.5 years). For MTBE they reported point decay rate constants of 0.44 per year (half-life of 1.6 years). In contrast, Peargin (2002) calculated rates from wells that were screened in areas with residual NAPL; the mean decay rate for MTBE was 0.04 per year (half life of 17 years) the rate for benzene was 0.14 per year (half life of 5 years). Newell (personal communication) calculated the following median point decay rate constants: 0.33 per year (2.1 year half-life) for 159 benzene plumes at service station sites in Texas; and 0.15 per year (4.7 year half-life) for 37 TCE plumes around the U.S.	For many BTEX plumes, *k* will be similar to biodegradation rates λ (on the order of 0.001 to 0.01 per day; see Figure 5) as the effects of dispersion and sorption will be small compared to biodegradation.	For BTEX compounds, 0.1 - 1 %/day (half-lives of 700 to 70 days)(Suarez and Rifai, 1999). Chlorinated solvent biodegradation rates may be lower than BTEX biodegradation rates at some sites (Figures 5 and 6). For more information about biodegradation rates for a variety of compounds, see Wiedemeier et al., 1999 and Suarez and Rifai, 1999.
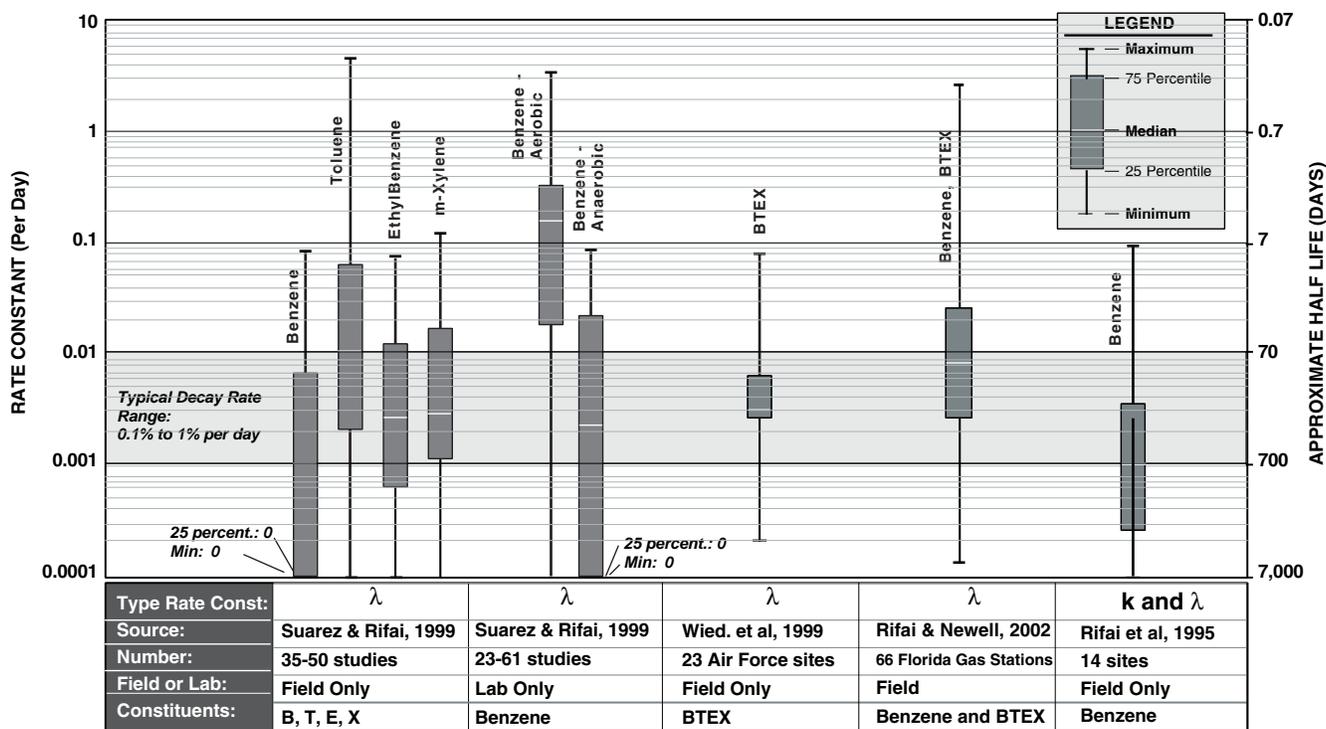
Figure 5. Biodegradation Rate Constants (λ) and Bulk Attenuation Rate Constants (*k*) for BTEX compounds from the literature. Source: Rifai and Newell, 2001.
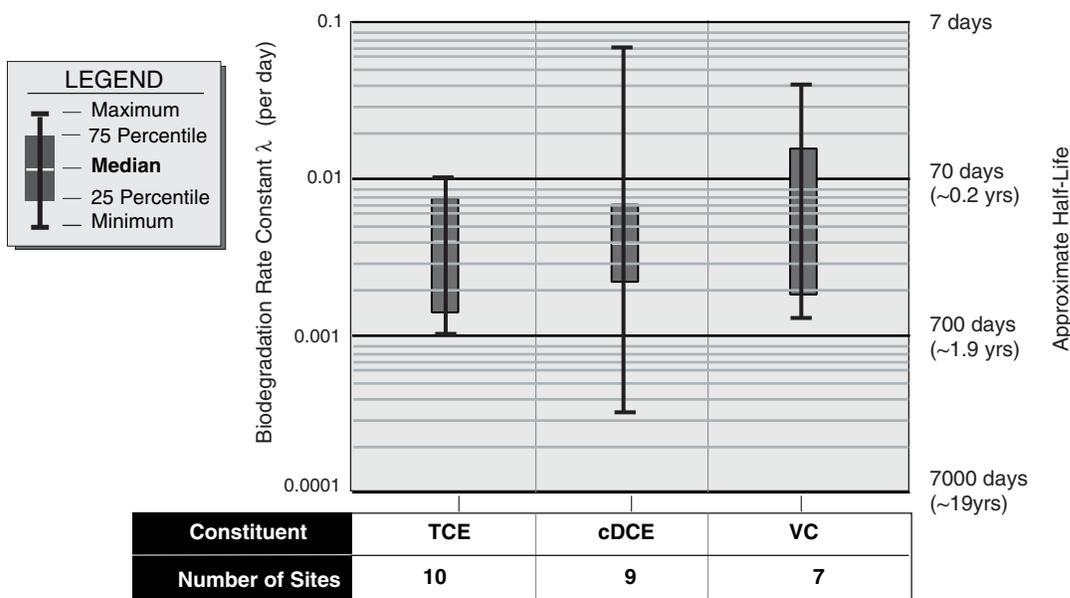
Figure 6. Biodegradation Rate Constants (λ) for Trichloroethene (TCE), cis-Dichloroethene (cDCE), and Vinyl Chloride (VC) compounds from BIOCHLOR modeling studies. Source: Aziz et al., 2000.

EXAMPLE 1. *Use of Concentration vs. Time Rate Constants (k_{point})*

INTRODUCTION: A leaking underground storage tank site in Elbert, Anystate, has a maximum source concentration of 1.800 mg/L of benzene at well MW-3. A remediation goal of 0.005 mg/L of benzene has been established. How long will it take for this site to reach the remediation goal using MNA with no active remediation? *(Data source: Mace et al. 1997)*

DATA:

The following are data from well MW-3 for the period 1986 to 1991.

DATE	Years Since 1/1/86	MW-3 Benzene (mg/L)
8/19/86	0.63	1.800
7/17/87	1.54	0.440
9/29/87	1.74	0.370
12/19/87	1.96	0.320
6/25/88	2.48	0.270
9/30/88	2.75	0.260
12/21/88	2.97	0.260
4/25/89	3.31	0.220
10/23/89	3.81	0.110
7/4/91	5.50	0.030
11/20/91	5.88	0.018

KEY POINT: The k_{point} degradation rate constant is +0.77 per year.
QUESTION: Why is the sign positive?
ANSWER: The rate constant is defined as a rate of degradation. The slope of the line is the rate of change. If the slope is negative, then concentrations are attenuating, and the rate of degradation is positive.

Calculation Tip: If you calculate the slope of the line with a calculator or with a spreadsheet, you need to change the sign to get a degradation rate constant.

$y = 1.9568e^{-0.7676x}$

Benzene MCL (0.005 mg/L)

CALCULATION: Construct a plot of concentration vs. time. Although the plot can be developed in many ways, the clearest way is to convert the time data to years using an arbitrary starting point (for this example we chose 1/1/86). By transforming the concentrations to natural log concentration, and using a spreadsheet or calculator to get the slope (-0.77) and intercept (0.67), the following equation of the line was generated:

$$\text{Ln (Conc. Benzene)} = \exp^{(0.67-0.77x)}$$

which resulted in the following rate equation:

$$\text{Benzene concentration (mg/L)} = 1.96 \text{ mg/L} * \exp^{(-0.77 \text{ yrs since } 1/1/86)}$$

where $k_{point} = +0.77$ per year.

Rearranging the equation:

$$\text{Time (years since 1/1/86)} = -\text{Ln [Conc. Benzene (mg/L) / 1.96] / 0.77}$$

For the case where the remediation goal is 0.005 mg/L benzene,

$$\text{Time (years since 1/1/86)} = -\text{Ln [0.005 / 1.96] / 0.77} = 7.7 \text{ years} = \textbf{late 1993}$$

A statistical analysis of the uncertainty involved in the calculation can be performed by determining the "one tailed" 90% confidence interval using the methods outlined in Appendix I. The "one tailed" 90% confidence limit on the time to remediation is a time that is no longer than 8.6 years from 1/1/86, or late 1994.

Plume Attenuation?
The concentration vs. time rate constant is positive, indicating that attenuation at this location (the source zone in this example) is occurring. The attenuation is probably due to weathering of the source caused by dissolution of benzene from a residual NAPL into flowing ground water. Raoult's Law predicts that weathering from dissolution will be a first-order process.

Plume Trends?
The concentration vs. time rate constant is positive, indicating that concentrations in this portion of the plume are going down and that at least a portion of the plume may be shrinking. However, from the information obtained at a single location, no conclusion can be drawn regarding the overall plume trend.

Plume Duration?
The concentration vs. time rate constant was used to show that if current trends hold then the plume will reach the clean-up goal in 1994. Note this assessment does not consider any other processes which could reduce the observed attenuation rate (i.e., changes in water levels, availability effects at low concentration as described by Kan et al., 1998, etc.).

Key Point:

A concentration vs. time rate constant is one of the best ways to estimate how long MNA (or any type of remediation system) might take to reach a clean-up goal. A second method is to perform a mass-based approach (i.e., see DuPont et al., 1998; Hyman and DuPont, 2001; Newell et al., 1996 or Chapter 2 of Wiedemeier et al., 1999).

EXAMPLE 2. *Use of Concentration vs. Distance Rate Constants (k)*

INTRODUCTION: This constant is estimated between wells along the inferred centerline of the plume. An MTBE plume at a former fuel farm located at a U.S. Coast Guard Base has a maximum source zone concentration of 1.740 mg/L of MTBE. The average calculated seepage velocity at the site was calculated to be 82 meters per year and the retardation factor, R, is assumed to be equal to one. For the purpose of this example, a clean-up goal of 0.030 mg/L was assumed. Most importantly, the site is strongly anaerobic, indicating that relatively high rates of MTBE biodegradation are possible. Is the MTBE plume attenuating? How far should it extend?

(source: Wilson et al., 2000).

DATA:
The following is data from wells along the plume centerline:

Well	Distance from Source(m)	MTBE Conc.(mg/L)
CPT-1	0	1.74
CPT-3	40	0.823
CPT-5	70	0.672
ESM-14	104	0.383
ESM-3	134	0.319
ESM-9	180	0.001
ESM-10	195	0.0097
GP-1	250	0.001

Key Point: The degradation rate constant k is + 0.0033 per year.

$y = 4.3561e^{-0.0333x}$
$R^2 = 0.828$
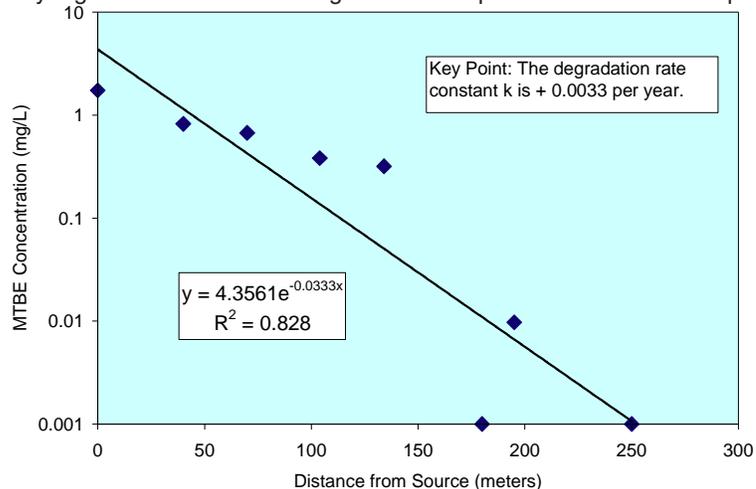
CALCULATION: First, plot the natural log of concentration vs. distance at a point in time and calculate the slope of the best-fit line using linear regression analysis, as shown above. The slope of the C vs. D plot is -0.033 per meter of travel.

Next, calculate the bulk attenuation rate constant, k, by multiplying the negative of the slope of the regression by the contaminant velocity. The contaminant velocity equals the seepage velocity divided by the retardation factor. In this case the retardation factor is 1, and the contaminant velocity is 82 meters per year. The bulk attenuation rate is (+0.033 per meter) * (82 meter per year) = 2.7 per yr. This corresponds to a dissolved-phase half-life of 0.26 yrs (0.26 yrs = 0.69 / 2.7 per yr) *after the MTBE leaves the source zone.*

To estimate the travel time required for the concentration of MTBE to attenuate to the cleanup goal, use the equation in Table 2. The travel time to reach the remediation goal at the down gradient margin of the plume is 1.5 years (1.5 yr = - Ln [0.030 mg/L/ 1.74 mg/L] / 2.7 per y). Based on the calculated attenuation rate, an MTBE source concentration of 1.74 mg/L, and a cleanup goal of 0.030 mg/L, the MTBE plume should extend 123 meters from the source (123 meters = 82 meters per yr * 1.5 yr travel time).

A sensitivity analysis can be performed on the rate estimates. See Appendix I for a discussion of confidence intervals. The one-tailed 95% confidence interval on the slope is -0.021 per foot. At a seepage velocity of 82 meters per year, this is equivalent to a concentration vs. distance rate constant (k) of 1.7 per year. The plume would require 2.4 years of travel in the aquifer to attenuate to the cleanup goal. At 95% confidence, the plume boundary would be no more than 200 meters from the source. The estimate of seepage velocity is also subject to uncertainty. A reasonable upper boundary on the seepage velocity at this site is 150 meters per year (Wilson et al., 2000). At the upper bound on seepage velocity, and at the 95% confidence interval on the slope, the MTBE plume would extend no more than 360 meters.

Plume Attenuation?	**Plume Trends?**	**Plume Duration?**
The calculated concentration vs. distance rate constant is positive, indicating that attenuation of dissolved MTBE is occurring after the MTBE leaves the source zone. The rate constant of 2.7 per year indicates that dissolved MTBE concentrations will be reduced by 50% every 0.25 yrs *after the MTBE leaves the source zone.* It does not indicate the entire plume will be reduced in concentration by 50% in 0.25 yrs.	In theory, the concentration vs. distance rate constant can provide supporting evidence that the plume may be showing relatively little change or shrinking in the future. However, an analysis of concentration vs. time data for all locations within an adequately delineated plume is a much more direct and robust method for estimating plume trends.	A concentration vs. distance rate constant is not useful for estimating plume duration (i.e., the time to reach a clean-up goal). A mass-based analysis by Wilson et al., 2000 indicated that 60 years might be required to reach the clean-up goal.

Key Point:

Concentration vs. distance rate constants cannot be used for estimating remediation time frames, and are only marginally useful for estimating plume trends. This type of rate constant is most useful to predict the boundaries of a plume. It can be used to plan the location of monitoring wells or sentinel wells. This rate constant is also used with other information to calculate the rate of biodegradation.

Example 3. Use of Biodegradation Rate Constants (λ).

IINTRODUCTION: A chlorinated solvent plume at the Cape Canaveral Air Force Base, Florida, has maximum source concentrations of 0.056 mg/L Tetrachloroethene (PCE), 15.8 mg/L Trichloroethene (TCE), 98.5 mg/L cis-Dichloroethene (DCE), and 3.08 mg/L Vinyl Chloride (VC), 33 years after the spill originally occurred. The calculated seepage velocity at the site is 111.7 ft per year. Based on the existing distribution of chlorinated solvents and degradation products, how far down the flow path will the plume extend when it eventually comes to a steady state? This example is based on the example in Appendix A.6 of the User's Manual for the BIOCHLOR natural attenuation decision support system (Aziz et al., 2000). This model and the user's guide can be downloaded at no cost from the EPA Center for Subsurface Modeling Support (CSMoS) at http://www.epa.gov/ada/csmos/models.html.

Well	Distance from Source (feet)	PCE (mg/L)	TCE (mg/L)	cis-DCE (mg/L)	VC (mg/L)
CCFTA2-9S	0	0.056	15.8	98.5	3.08
MP-3	560	<0.001	0.220	3.48	3.08
CPT-4	650	ND	0.0165	0.776	0.797
MP-6	930	<0.001	0.0243	1.2	2.52
MP-4s	1085	<0.001	<0.001	0.556	5.02

CALCULATION: The following approach was used to determine biodegradation rate constants for each of the chlorinated solvents using a solute transport model:

Step 1: Perform parameter estimation and enter data into model.

Step 2: By trial-and-error, adjust the first-order biodegradation rate constants (λ) to match the observed site data. The resulting first-order biodegradation rate constant for PCE was 2.0 per year (half-life of 0.34 years), for TCE was 1.0 per year (half-life was 0.7 years), for cis-DCE was 0.7 per year (half-life 1.0 years) and for VC was 0.4 per year (half- life of 1.7 years).

Step 3: Run the simulation forward in time until it comes to an apparent steady state.

Step 4: Compare the simulated distribution of contaminants to the existing data used to calibrate the model. As discussed in Example 1, attenuation rates for declining concentration are positive values. When compared to values in the literature (see Figures 5 and 6), the values appear to be reasonable. All plume lengths were projected to the boundary defined by the MCL for Vinyl Chloride. Available data to calibrate the model extended 1085 ft from the source. The model was calibrated to the first 33 years of the plume. When the simulation was extended to 100 years the projections reached a steady state. At steady-state, there was no significant increase in the length of the TCE plume, but the cis-DCE plume was approximately twice as long at the time data available for calibration were collected, and the VC plume was approximately three times as long.
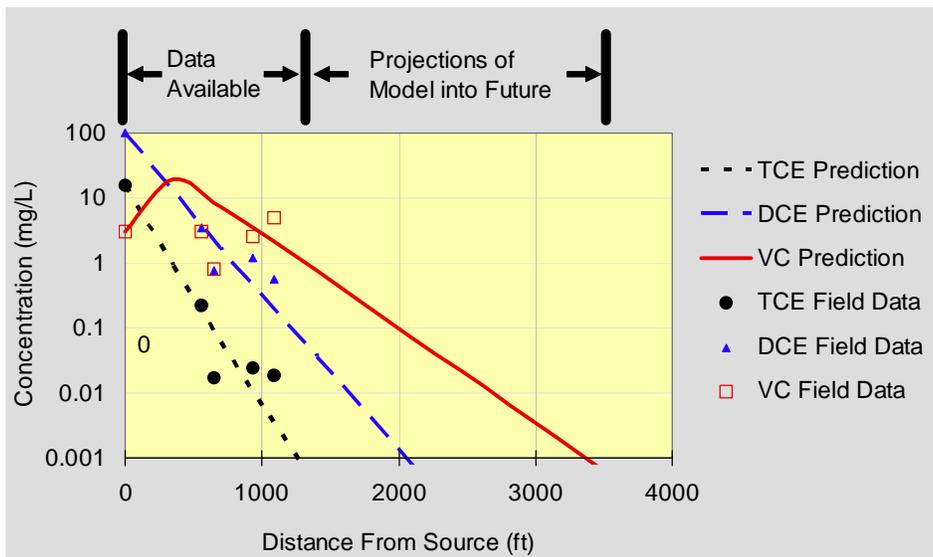
Plume Attenuation?	**Plume Trends?**	**Plume Duration?**
The calculated biodegradation rate constant is positive, indicating that biodegradation of dissolved chlorinated solvents *is occurring after the solvents leave the source zone.* PCE and TCE had the highest rates, while VC had the lowest rate at this site.	The screening model used biodegradation rate constants to project the future distribution of PCE, TCE, cis-DCE, and VC. The model projects relatively little change in the PCE, and TCE plumes, but the model predicts that the cis-DCE and VC plumes are expanding. To confirm the true behavior of the cis-DCE and VC plume, it may be necessary to install more monitoring wells to adequately delineate the plume, and collect data on concentration vs. time in all the wells in the plume.	A biodegradation rate constant is not useful for estimating the duration of the plume (i.e., the time to reach a clean-up goal).

Key Point:

Biodegradation rate constants cannot be used for estimating remediation time frames, but are useful for identifying possible trends in the behavior of plumes using mathematical models.

Appendix I. Uncertainty in Rate Calculations

Using Statistics to Estimate the Time Frame to Achieve Remediation Objectives

As with any remediation method, one of the fundamental questions that arises is "How much time will be required before remediation objectives are achieved?" At the current state of practice, the only practical approach available uses a statistical analysis of long-term monitoring data from wells in the source area of the contaminant plume. Many practitioners will calculate the Pearson product moment correlation coefficient (R^2) for the regression used to extract the Point Decay Rate constant (k_{point}). If the coefficient is near one (e.g., greater than 0.9 or 0.95), the regression is accepted as being useful in a qualitative way. There are two problems with this approach; it does not allow the user to select a level of confidence for the comparison, and it does not give more validity to regressions with many points compared to regressions with only a few points.

The slope of the regression is the rate constant. A better approach is to calculate a confidence interval on the slope of the regression. The following data from Kolhatkar et al., 2000 will be used to illustrate this approach. They collected long-term ground-water monitoring data from three wells at a gasoline release site in New Jersey. Their original data displayed extreme oscillations with concentrations bouncing from a high value down to the analytical detection limit of 1µg/L, and then back to a high value over sequential sampling intervals. Although the scatter in the data set is typical of the variation seen at many other sites, the influence of these outliers on the statistical estimate of the rate of attenuation was removed by editing the data set to remove those points where the concentration of MTBE was less than the detection limit.

Table I-1. Sources of Uncertainty in Calculated Rate Constants

	Rate Constant	Problem	Recommendation
	Point Decay Rate (k_{point})	Wells not in strongest source area may not give representative indication of how long entire plume will persist.	Characterize source with several wells. Estimate and report uncertainty in final result (estimated time to reach clean-up standards).
	Bulk Attenuation Rate Constant (k)	Wells not on centerline of plume can give misleading indications about concentration profile in plume.	Use a well-designed monitoring well network with transects of wells in rows across the plume rather than one set of wells down the inferred centerline. Estimate and report uncertainty in final result (estimated plume length).
	Biodegradation Rate Constant (λ)	A poorly designed monitoring well network may give misleading information about source strength, source size, and centerline plume concentrations used for calibration.	The source and plume need to be well characterized to ensure representative modeling results. Perform sensitivity analysis on model.
	Point Decay Rate (k_{point})	Can introduce additional scatter in data used to develop k_{point} rate constant.	Address as part of an uncertainty calculation (see below). For strong seasonal effects, use of data from the same season can be considered.
	Bulk Attenuation Rate Constant (k)	Typically not a problem as all data are collected at the same time.	Not applicable.
	Biodegradation Rate Constant (λ)	Can be a problem if seasonal effects are significant and the data used for calibration are not collected (concentration vs. distance) at the same time.	For strong seasonal effects, use data from same season to help ensure representative modeling results. Perform sensitivity analysis on model.
	Bulk Attenuation Rate Constant (k)	Increases overall uncertainty in calculation.	Average results from multiple seepage estimates along plume centerline. Improve seepage velocity estimate. Estimate and report uncertainty in final result (estimated plume length).
	All rate constant calculations	Increases apparent uncertainty.	Use worst-case data. Use transects to capture plume heterogeneity. For regression-based rate constants (k and k_{point}), estimate and report uncertainty in final result. For modeling studies designed to determine λ, perform sensitivity analysis on model by changing key variables to their upper and lower expected range and evaluate how modeling results change.

Because there is natural scatter in the long-term monitoring data, there is uncertainty in the estimate of the Point Decay Rate (k_{point}), and in the projected time frame to achieve cleanup in that monitoring well. To account for this uncertainty, a confidence interval was calculated for each estimate of the Point Decay Rate (k_{point}) at a pre-determined level of confidence of 90% and 95%. The level of confidence is simply the probability that the true rate is contained within the calculated confidence interval. A confidence level of 90% is reasonable for many sites. At other sites, a more stringent confidence level (e.g., 95%) may be more appropriate, depending upon the level of risk that is acceptable.

In most applications of regression, the user wishes to calculate both an upper boundary and lower boundary on the confidence interval that will contain the true rate at the pre-determined level of confidence. This is termed a "two tailed" confidence interval because the possibility of error (the tail of the probability frequency distribution) is distributed between rates above the upper boundary and below the lower boundary of the confidence interval. As a consequence, tables of critical values in statistical reference books and computer applications provide a "two-tailed" confidence interval. At a level of confidence of 80%, the estimate will be in error 20% of the time. The true rate will be contained within the

calculated confidence interval 80% of the time, 10% of the time the true rate will be faster than the upper boundary of the confidence interval, and 10% of the time the true rate will be slower than the lower boundary of the confidence interval. Using the data provided above from MW-5, the slope of a regression of the natural logarithm of concentration of MTBE on time is -0.188 per year. The Point Decay Rate (k_{point}) is +0.188 per year. The boundaries of the "two tailed" confidence interval on the rate at 80% confidence are 0.248 per year and 0.127 per year. This means that 80% of the time the true rate will be between 0.248 and 0.127 per year, that 10% of the time the true rate is greater than 0.248 per year, and 10% of the time the true rate is less than 0.127 per year. The true rate will be greater than 0.127 per year 90% of the time.

There is little value in estimating the shortest possible time that would be required to reach the goals for cleanup; remedial options are compared and evaluated based on the greatest time required to reach goals. At the selected level of confidence, all the possibility of error should be assigned to rates that are slower than the lower boundary of the confidence interval. This is a "one-tailed" confidence level; it includes all true rates that are faster than the lower boundary of the confidence interval. A "one tailed"

Table I-2. MTBE Concentrations in the Three Most Contaminated Monitoring Wells at a Gasoline Spill Site

	MW-5	MW-6	MW-11
Date	Concentration (µg/liter)	Concentration (µg/liter)	Concentration (µg/liter)
9/17/93	1,900	270	
9/23/94	1,800	200	2200
5/17/96	1,300	120	880
8/10/96	980	120	
11/7/96	620	66	660
12/8/97	500		339
3/27/98	635	71.2	426
7/23/98	470		419
9/18/98	1,210	44	
12/16/98	379		144
3/1/99	700	42.2	123
6/21/99	574		464
9/7/99	792	43.2	195
9/7/99	1,050		155
12/30/99	525		220
3/20/00	501	36	173
6/22/00	420	51.2	146

confidence interval can be calculated as the slower of the two confidence intervals from a "two-tailed" test that has twice the uncertainty. In the example above, where "two tailed" confidence intervals were calculated for a confidence level of 80%, the true rate will be greater than a rate of 0.127 per year 90% of the time. The "one tailed" confidence intervals reported in the table below were calculated in this fashion. Monitoring well MW-5 has the highest concentration of MTBE and the lowest Point Decay Rate, and can reasonably be expected to be the last monitoring well to reach the goal. The other monitoring wells should reach the goal much sooner; the best estimate of the lifetime of the plume is the expected lifetime of MTBE in MW-5.

Note that for a given number of observations, as the level of confidence is increased, the interval that is expected to contain the real value for the rate constant increases as well. As the level of confidence increases, the lower boundary on the rate constant decreases, and the projected time required to meet the clean-up goal increases. In the examples presented above, the estimated rate of natural attenuation of MTBE in MW-5 is 0.188 per year, which requires 16 years to attain a concentration of 20 µg/L. At a 90% confidence level, the lower boundary of the confidence interval is 0.127 per year, which requires 24 years to meet the goal. At a 95% confidence level, the lower boundary is 0.109 per year, which requires 28 years to reach the goal. At the 95% confidence level the upper bound of the time expected to reach the clean-up goal has increased by a factor of almost two (from 16 years to 28 years). This does not necessarily mean that the actual time to achieve cleanup will be 28 years; it simply means that the length of time that will actually be required is estimated to be no more than 28 years at a 95% level of confidence.

At many sites, the long-term monitoring data show that the concentration of MTBE actually increases over time. At other sites, the general trend in the concentration of MTBE may be down, but there is a great deal of variation in the data. These variations in concentrations over time are not necessarily errors in sampling and analysis of ground water. In many cases they reflect real changes in the plume caused by seasonal variations in precipitation. These variations are a natural property of plume. If the variation is large enough, one boundary of the "two tailed"

confidence interval will be a positive number and the other boundary will be a negative number. When zero is included in the confidence interval on the rate, there is no evidence in the data that the true rate is different from zero. If this is the case, it is possible that attenuation is occurring in that particular well over time, but the monitoring data do not present evidence that attenuation is occurring at the predetermined level of confidence. At the predetermined level of confidence, it is impossible to predict how long it will take to reach the clean-up goals.

The ability to extract a rate of attenuation from long-term monitoring data is related to the number of measurements, and the time interval over which they are collected. As an example, the rate of attenuation extracted from the last three years of monitoring data for well MW-5 (3/27/1998 to 6/22/2000) is 0.106 per year, but the "one tailed" 90% confidence interval is all rates greater than -0.125 per year. The confidence interval includes zero. If only these three years of data were available, there would be no evidence of natural attenuation of MTBE in well MW-5 at 90% confidence. The rate extracted from the last four years of data (5/17/1996 to 6/22/2000) is 0.130 per year. The 90% confidence interval on the rate (0.0302 per year) would reach the clean-up goal in 100 years. The rate extracted using all the seven years of monitoring data is 0.188 per year. The 90% confidence interval on the rate would reach cleanup in 24 years. A few extra years of monitoring data have a strong influence on the ability to extract useful rate constants.

Key Point:

The Point Decay Rate (k_{point}) can be used to project the time required for reaching a clean-up goal. However, there are a number of points to keep in mind. First, an appreciable record of long-term monitoring data must be available to make a statistically valid projection of the rate of natural attenuation. As a practical matter, it is difficult to extract rate constants that are statistically significant with fewer than six sampling dates, or with a sampling interval of less than three years. Second, it is unrealistic to expect just a few years of monitoring data to accurately predict plume behavior several decades into the future. Third, it is important to realize that these estimates are merely estimates and that the true rate may change over time.

Table I-3. Point Decay Rate (k_{point}) of Attenuation of MTBE in Monitoring Wells and the Projected Time Required to Reach a Clean-Up Goal of 20 mg/L as Calculated from the Long-Term Monitoring Data for the Wells

Well	MTBE (µg/L)		Estimated rate and time required		Rate and time significant at 90% confidence		Rate and time significant at 95% confidence	
	First Sample 1993	Last Sample 2000	*Rate (per year)*	*Time (years)*	*Rate (per year)*	*Time (years)*	*Rate (per year)*	*Time (years)*
MW-5	1900	420	0.188	16	0.127	24	0.109	28
MW-11	2200	146	0.453	4.4	0.365	5.4	0.337	5.9
MW-6	270	51.2	0.29	3.2	0.246	3.8	0.231	3.8

Appendix II. Contaminant Concentration Attenuation Downgradient from Source Areas as a Function of Dispersion, Sorption, and Biodegradation

INTRODUCTION: The Domenico solution to the advection-dispersion-biodegradation equation along the centerline of a plume was applied to a hypothetical case to illustrate the impact of the different attenuation parameters on the overall bulk attenuation rate. The Domenico solution is given by

$$C(x,t) = \frac{C_0}{2} \exp\left[\frac{x}{2\alpha_x}\left(1 - \sqrt{1 + \frac{4\lambda\alpha_x}{v}}\right)\right] \text{erfc}\left(\frac{x - vt\sqrt{1 + \frac{4\lambda\alpha_x}{v}}}{2\sqrt{\alpha_x vt}}\right) \text{erf}\left(\frac{Y}{2\sqrt{\alpha_y x}}\right)$$

where C_o is the initial concentration, α_x is the longitudinal dispersivity, α_y is the transverse dispersivity, λ is the biodegradation rate, t is time, x is distance from the source, v is the retarded ground-water velocity (i.e., $v=v_s/R$), and Y is source width.

DATA: The following are the parameters assumed for this example:

v_s = 100 ft/yr (median value from the HGDB database (Newell et al., 1990))
Y = 40 ft
t = 10 years
α_y = 0.1 α_x
b = 10 ft (source thickness used for the Bioscreen runs)

CALCULATION: Four different scenarios were considered to estimate the effect of the different parameters on the overall attenuation rate: 1) the only process acting at the plume is dispersion (α_x = 100 ft); 2) previous scenario plus the effect of sorption (R=5); 3) dispersion, sorption, and biodegradation (λ=0.2 per yr) are acting; and 4) previous scenario plus the effect of source decay (k_{source}= 0.139 per yr).

For each scenario, the Domenico solution was applied to obtain concentrations along the centerline of the plume. Next, concentrations vs. distance were plotted and data were fit with an exponential equation (first-order model). The slopes of the C vs. D plots were 0.002, 0.0106, 0.0124, and 0.0237/ft for scenarios 1, 2, 3, and 4, respectively. Finally, the bulk attenuation rate constant, k, for each scenario was calculated by multiplying the slope by the contaminant velocity (100 ft/yr/retardation factor). This calculation yielded bulk attenuation rates equal to 0.2, 0.212, 0.248, and 0.474/year for scenarios 1, 2, 3, and 4, respectively. These values correspond to dissolved-phase half-lives of 3.5, 3.3, 2.8 and 1.5 years after the contaminant leaves the source zone.
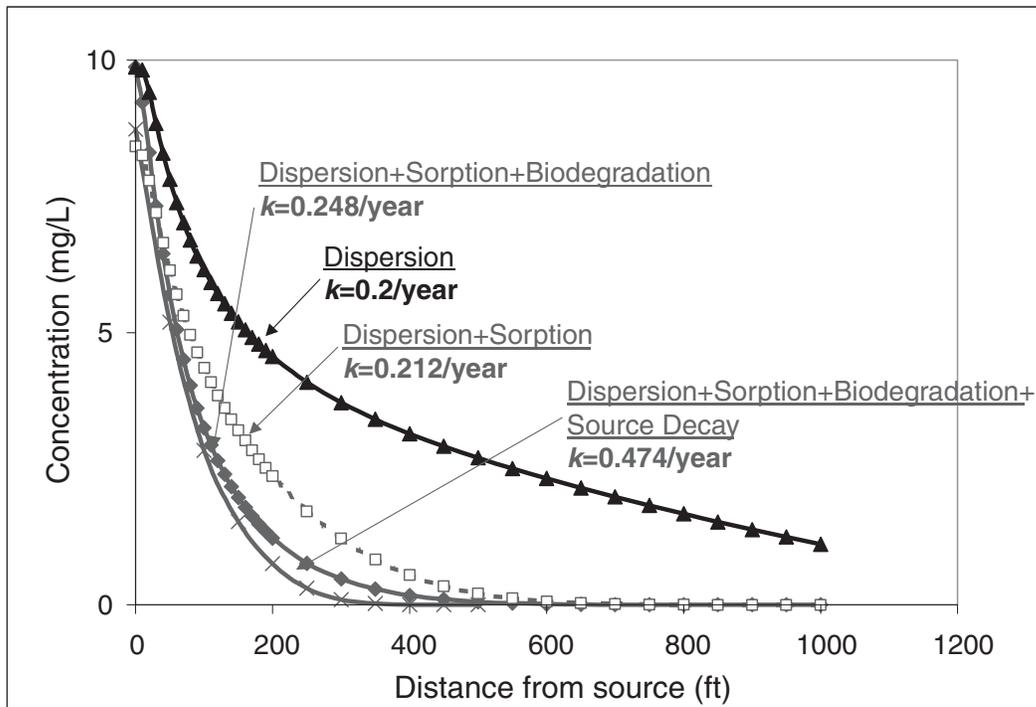
This example illustrates incremental attenuation impacts of the various attenuation processes and how the overall bulk rates change as a result (i.e., the more processes present at a given site, the higher the bulk attenuation rate). The effect of individual parameters on the attenuation rate is discussed below:

Bulk Attenuation Rate (*k*) as a Function of Longitudinal Dispersivity (α_x)

The figures below show the calculation of k for different dispersivity values as well as a resulting plot of bulk attenuation rate as a function of longitudinal dispersivity. The transverse dispersivity (α_y) was set to 10% of the longitudinal dispersivity (α_x), the vertical dispersivity (α_z) was set to 10% of the transverse dispersivity (α_y), and $t = 30$ years. The slopes of the concentration vs. distance plots were multiplied by the contaminant velocity to obtain bulk attenuation rates. This type of calculation assumes that the plume is at steady-state. The figures below suggest that the bulk attenuation rate (k) increases as dispersivity increases.
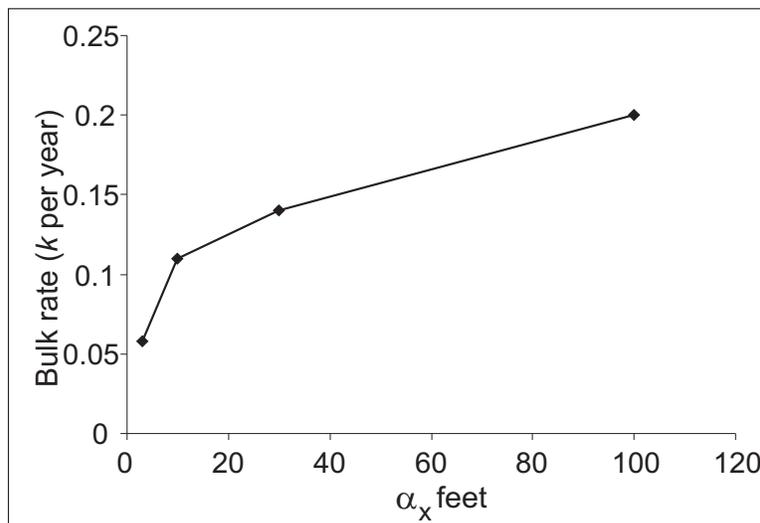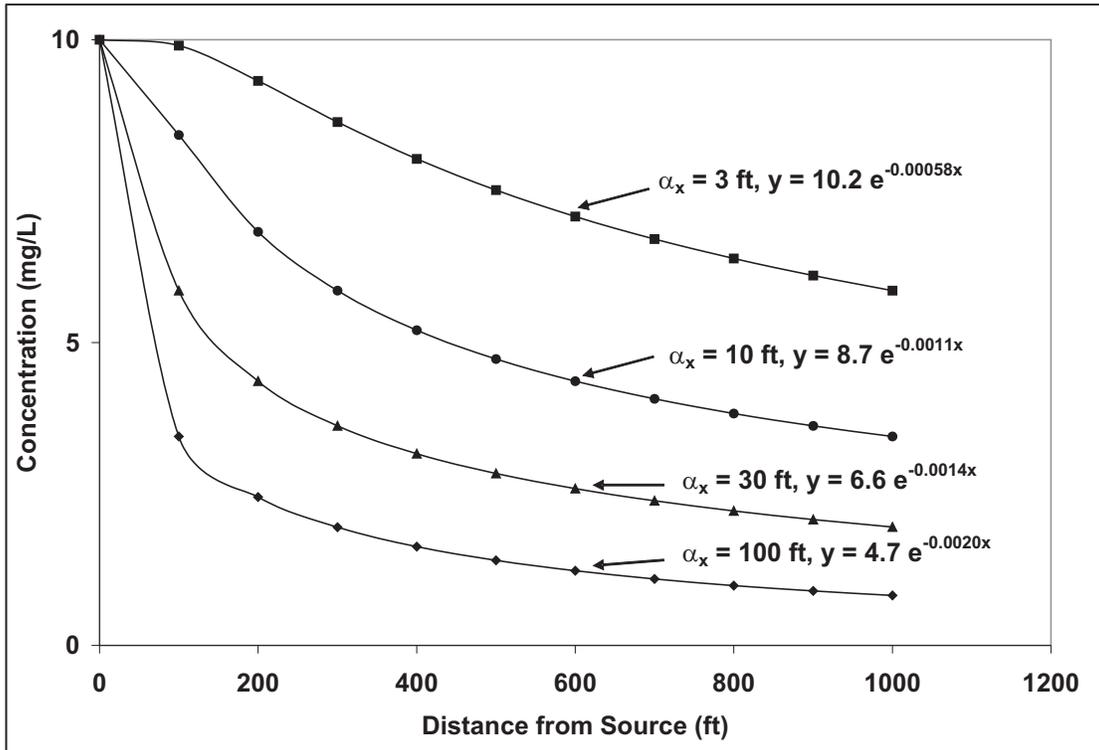
Bulk Attenuation Rate (k) as a Function of Sorption prior to Equilibrium.

When a plume comes to a steady state, sorption no longer removes contaminants from ground water, and there is no effect of sorption on the bulk attenuation rate (k). Prior to equilibrium, sorption removes contaminants from the ground water and contributes to the bulk attenuation rate. The effect of sorption on the bulk attenuation rate was evaluated by calculating k for different retardation factors and plotting the resulting k values as a function of R as illustrated in the figures below. For this analysis a longitudinal dispersivity of 100 ft was assumed, and t = 10 years. In this case, the slopes of the concentration vs. distance plots were multiplied by the seepage velocity rather than the contaminant velocity to obtain bulk attenuation rates, since retardation was already included in the Domenico calculation. It can be concluded that with all the other parameters constant, the bulk attenuation rate is roughly proportional to the retardation factor.

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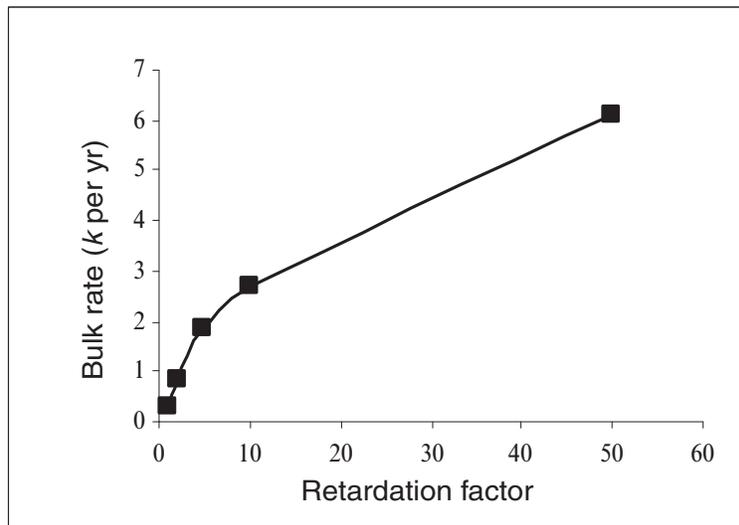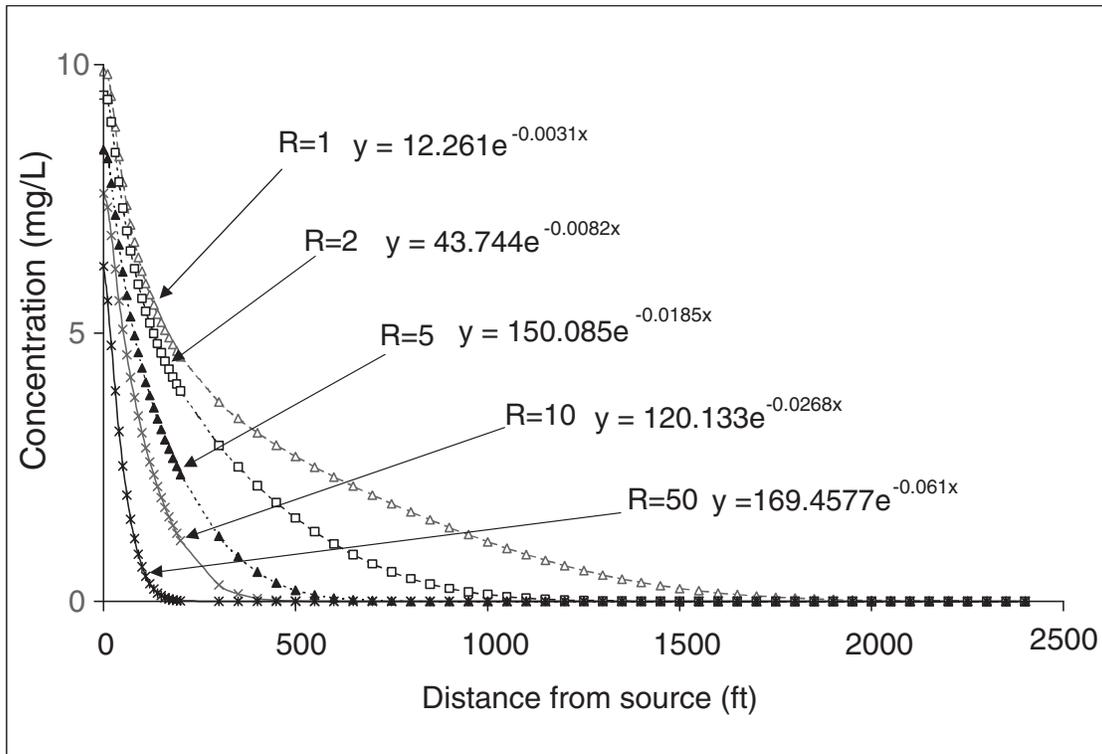
Bulk Attenuation Rate (*k*) as a Function of Biodegradation Rate (λ)

Bulk attenuation rates for first-order biodegradation rates within the range 0 to 0.5/year were estimated and a plot of *k* versus λ was prepared to illustrate the impact of this parameter on the overall attenuation rate. For this analysis a longitudinal dispersivity of and a retardation factor equal to 1 (no sorption) were assumed. As shown in the following figures, with all the other parameters being constant, the bulk attenuation rate increases as the biodegradation rate increases.
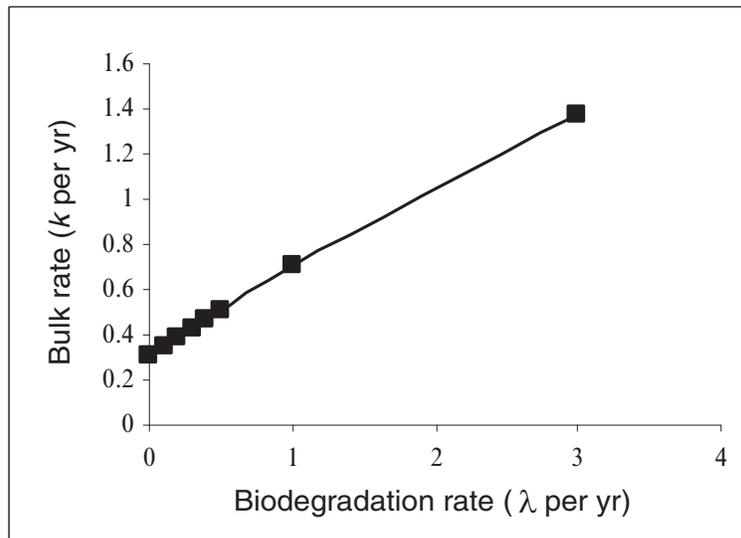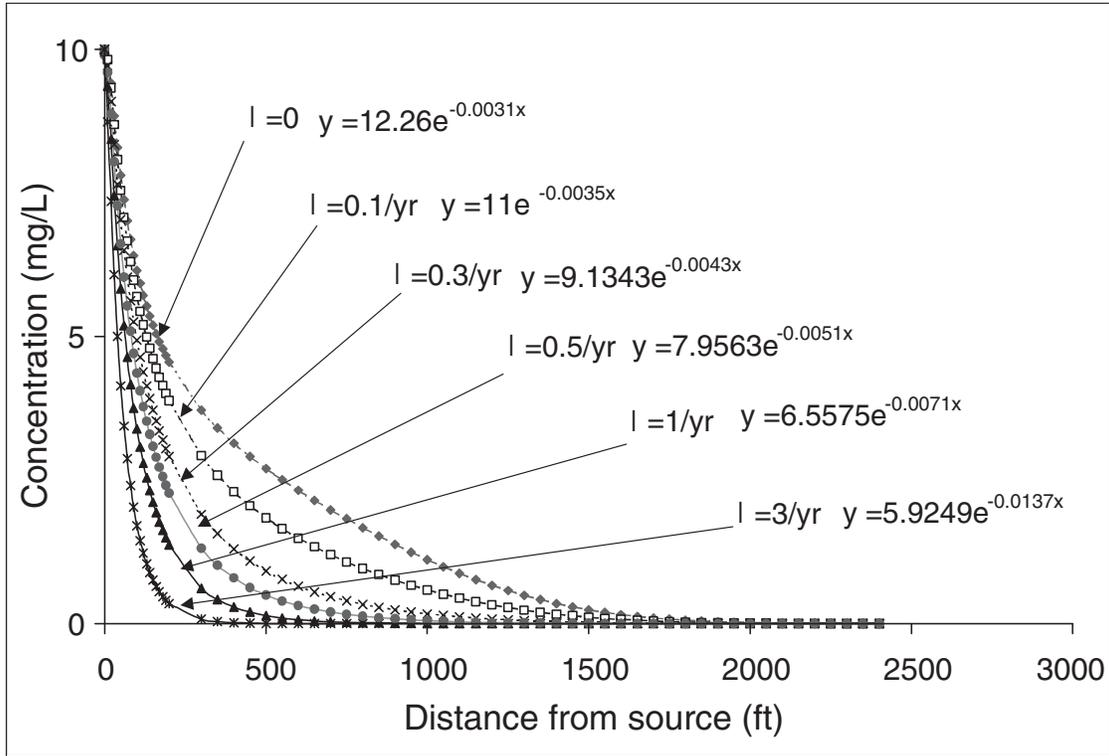
Bulk Attenuation Rate (k) as a Function of Source Decay Rate (k_{source})

The figures below show the calculation of k for source decay rates varying between 0 and 0.69/yr as well as the resulting plot of bulk attenuation rate as a function of k_{source}. The effect of source decay was evaluated using the Bioscreen model (Newell et al., 1996). For this scenario, a longitudinal dispersivity of 100 ft and no sorption nor biodegradation were assumed. It can be inferred that the bulk attenuation rate decreases as source decay rate increases.

The concentration versus distance plot shows curves for:

$k_{source} = 0 \quad y = 5.9929e^{-0.0038x}$

$k_{source} = 0.0139/\text{yr} \quad y = 5.231e^{-0.0037x}$

$k_{source} = 0.069/\text{yr} \quad y = 3.038e^{-0.0031x}$

$k_{source} = 0.139/\text{yr} \quad y = 1.5404e^{-0.0024x}$

$k_{source} = 0.346/\text{yr} \quad y = 0.2007e^{-0.0004x}$

$$k \propto \frac{1}{k_{source}}$$
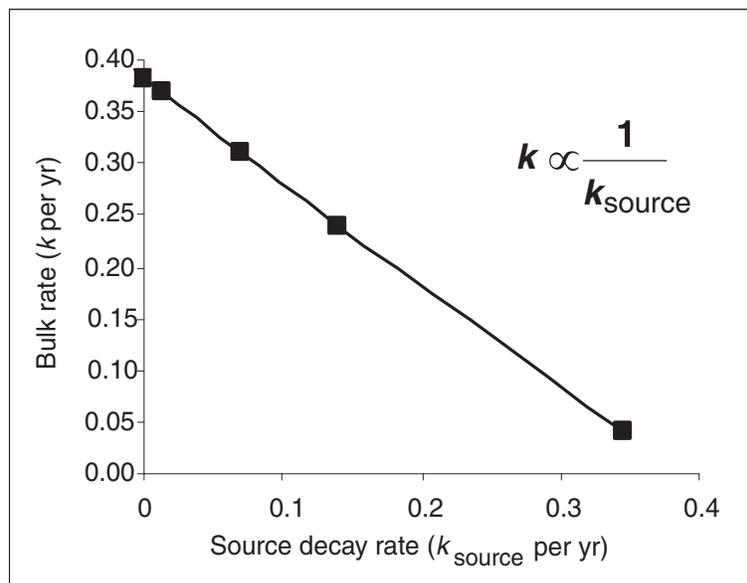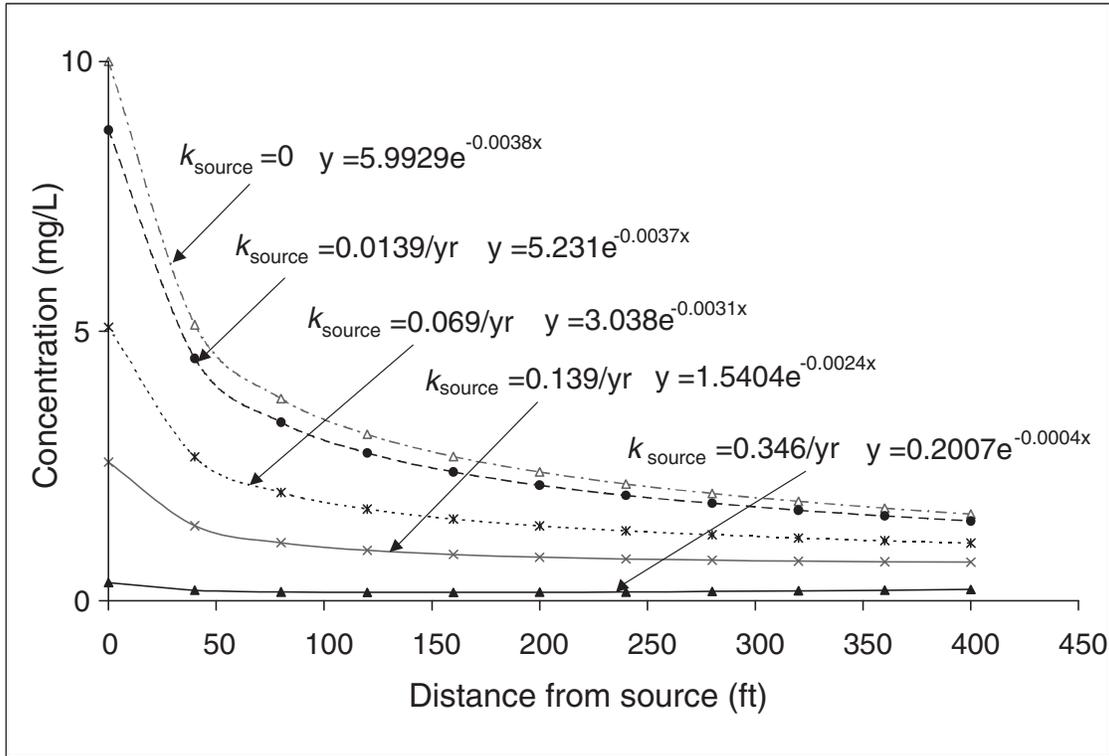
Appendix III. Effect of Dispersion, Sorption, Biodegradation, and Source Decay on Concentration vs. Time Profiles

INTRODUCTION: Concentration versus time profiles for a hypothetical case were generated using the Domenico solution to the advection-dispersion-biodegradation equation along the centerline of a plume to illustrate the impact of the different attenuation parameters on the point attenuation rate at two different locations, one near the source area and the other 200 ft downgradient from the source.

DATA: The parameters assumed for this example are as follows:

v_s = 100 ft/yr (median value from the HGDB database (Newell et al., 1990)), Y = 40 ft , α_y = 0.1 α_x, b = 10 ft (source thickness used for the Bioscreen runs)

CALCULATION: Four different scenarios were considered to estimate the effect of the different parameters on the overall attenuation rate: 1) the only process acting at the plume is dispersion (α_x = 100 ft); 2) previous scenario plus the effect of sorption (R=5); 3) dispersion, sorption, and biodegradation (λ=0.2 per yr) are acting; and 4) previous scenario plus the effect of source decay (k_{source}= 0.139 per yr).

For each scenario, the Domenico solution was applied to obtain concentrations at two locations: one near the source area (X=20 ft) and the other at a point located 200 ft downgradient from the source as a function of time. As illustrated in the figures below, when running Concentration vs. Time profiles, a decline in concentration near the source is not observed unless the source is decaying. Without source decay, the concentrations increase until they reach a steady-state maximum value and thereafter remain constant even when dispersion, sorption, and biodegradation are present at a site (scenarios 1, 2, and 3). On the other hand, when source decay is included, concentrations increase up to a maximum and decrease with time. (Note the two graphs have different scales).

Near source location
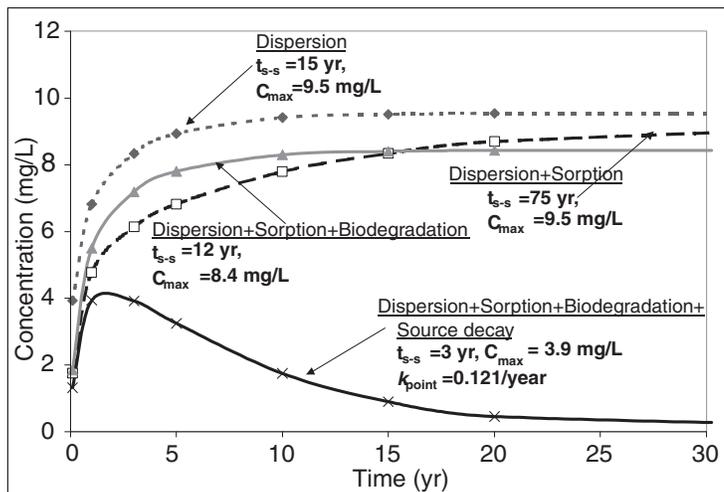
It should be noted that while concentrations do not show attenuation as a function of time without source decay, a decrease in the maximum concentration occurs as a result of the various attenuation processes. For instance, the steady-state concentrations for the well located 20 ft from the source area were 9.5 mg/L when only dispersion was present, 9.5 mg/L when both sorption and dispersion were acting, 8.4 mg/L when dispersion, sorption and biodegradation were present, and 3.9 when source decay was included. Similarly, for the point located 200 ft from the source, maximum concentrations were 4.7, 4.7, 1.3, and 0.6 mg/L for scenarios 1, 2, 3, and 4, respectively. In other words, the more processes acting at a given site, the lower the maximum concentration observed. In addition, the presence of different processes impacts the time required to reach steady-state. For the source location, the time to steady-state was 15, 75, 12, and 3 years for scenarios 1, 2, 3, and 4, respectively; whereas for the downgradient location, the time to steady-state was 15, 100, 12, and 10 years for scenarios 1 to 4.
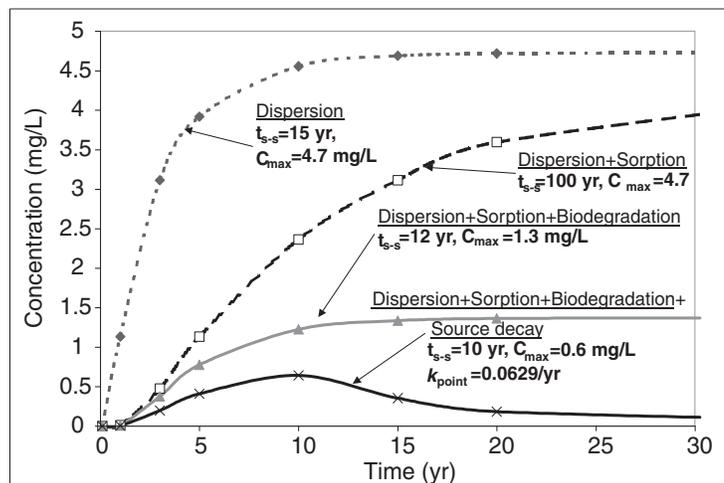
This example illustrates the impacts of the various attenuation processes on the maximum concentrations observed at different locations within a plume. It can be inferred that the more processes present at a given site, the lower the maximum concentration observed. The effect of individual parameters on the Concentration vs. Time profiles is discussed below.

Downgradient location

Effect of Longitudinal Dispersivity (α$_x$) on Concentration vs. Time Profiles

The figures below show concentration vs. time profiles for different dispersivity values for a source location (X=20 ft) and a downgradient location (X=200 ft). The maximum concentration decreases as the longitudinal dispersivity increases and the time required to reach steady-state increases as dispersivity increases.
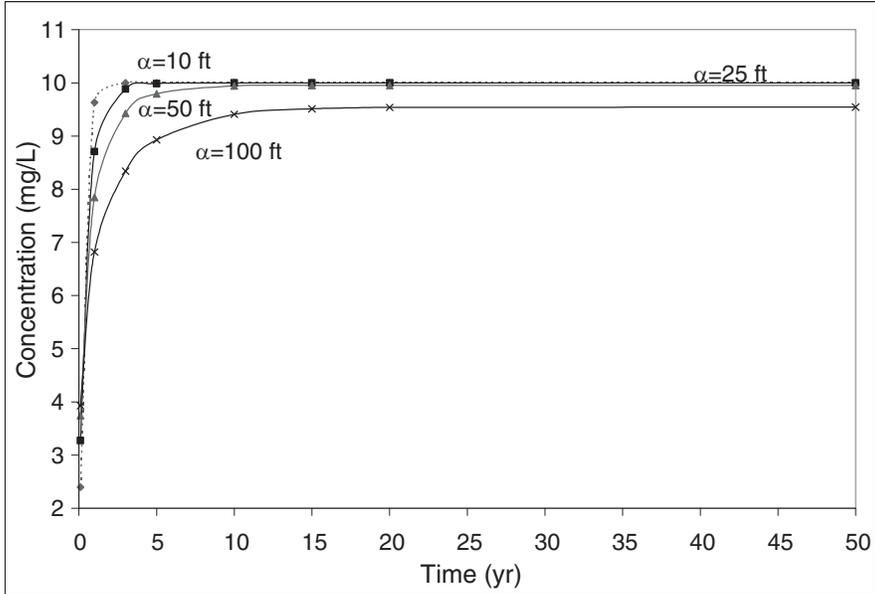
Near source location
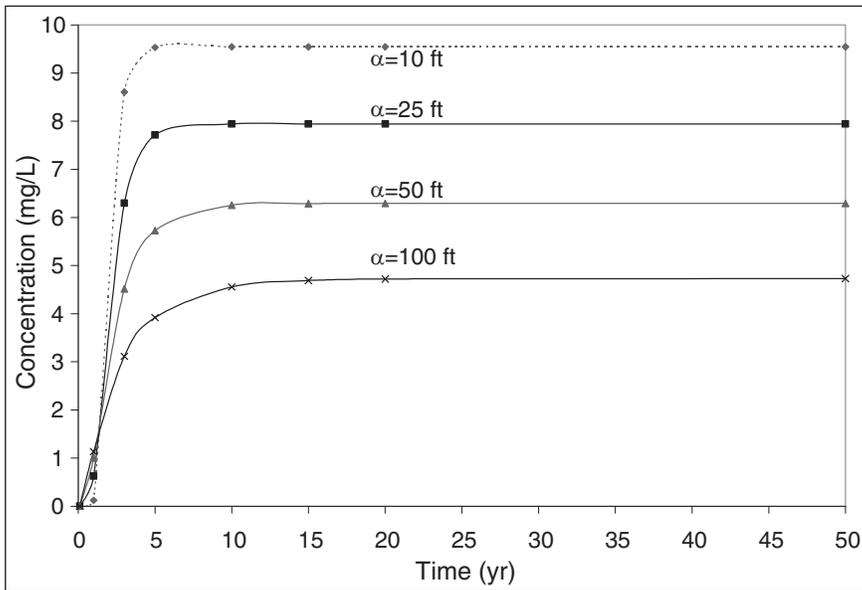
Downgradient location

Effect of Sorption on Concentration vs. Time Profiles

Changes in Concentration vs. Time profiles as a result of sorption were evaluated by plotting the profiles at the source and downgradient locations for different retardation factors. For this analysis a longitudinal dispersivity of 100 ft was assumed. As can be seen in the figures below, the time required to reach steady-state increases as the retardation factor increases. Sorption, however, does not change the steady-state concentration. (Note the two graphs have different scales.)
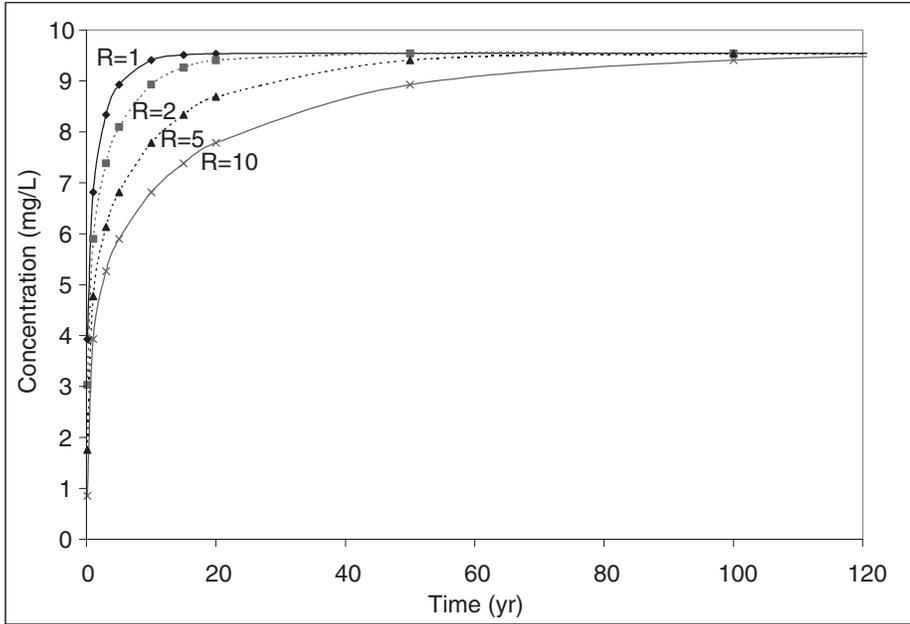
Near source location
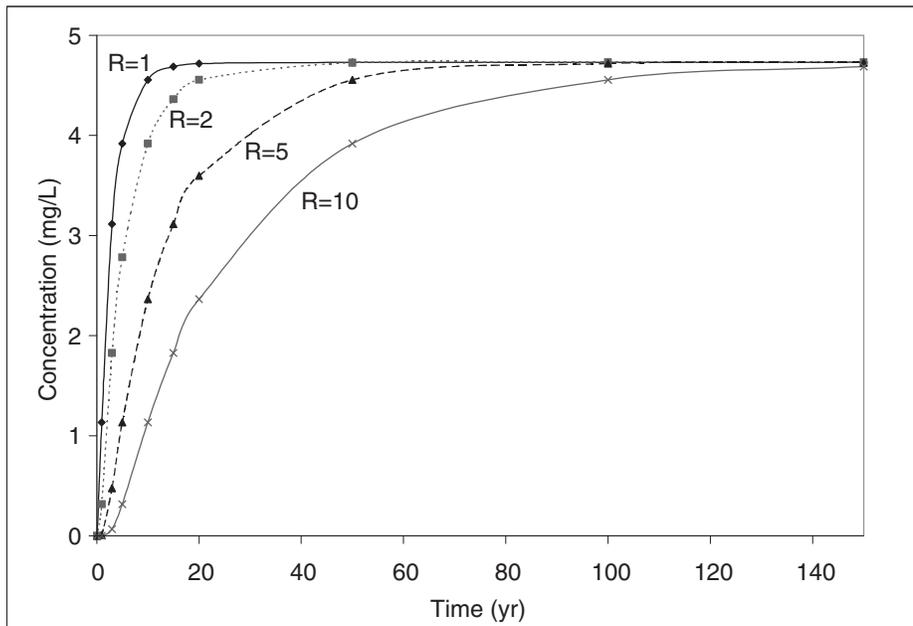
Downgradient location

Effect of Biodegradation (λ) on Concentration vs. Time Profiles

The figures below show concentration vs. time profiles for different biodegradation rates for both the source and downgradient locations. For this analysis a longitudinal dispersivity of 100 ft and a retardation factor equal to 1 (no sorption) were assumed. As shown below, the higher the biodegradation rate, the lower the maximum concentration and the shorter the time required to reach steady-state. (Note the two graphs have different scales.)
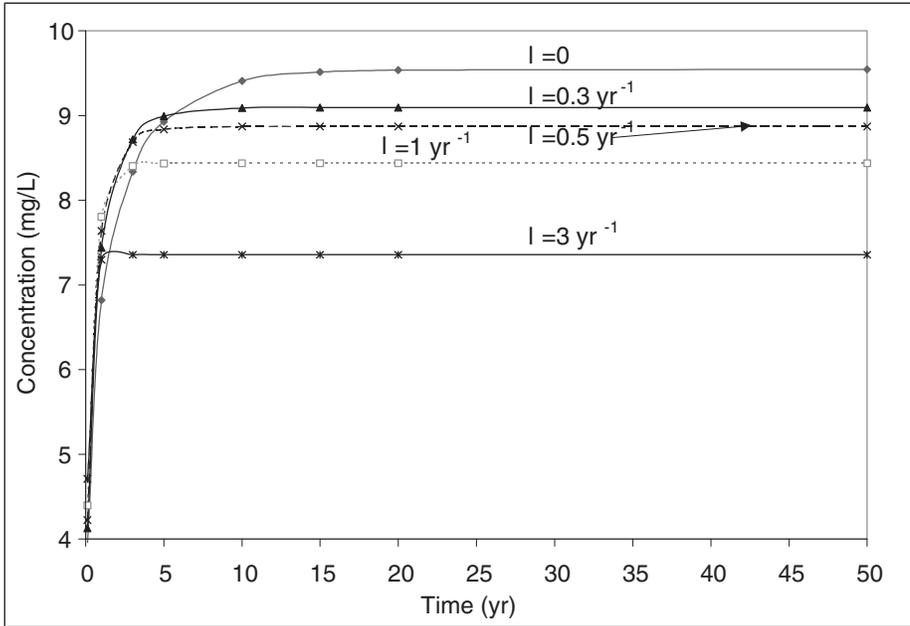
Near source location
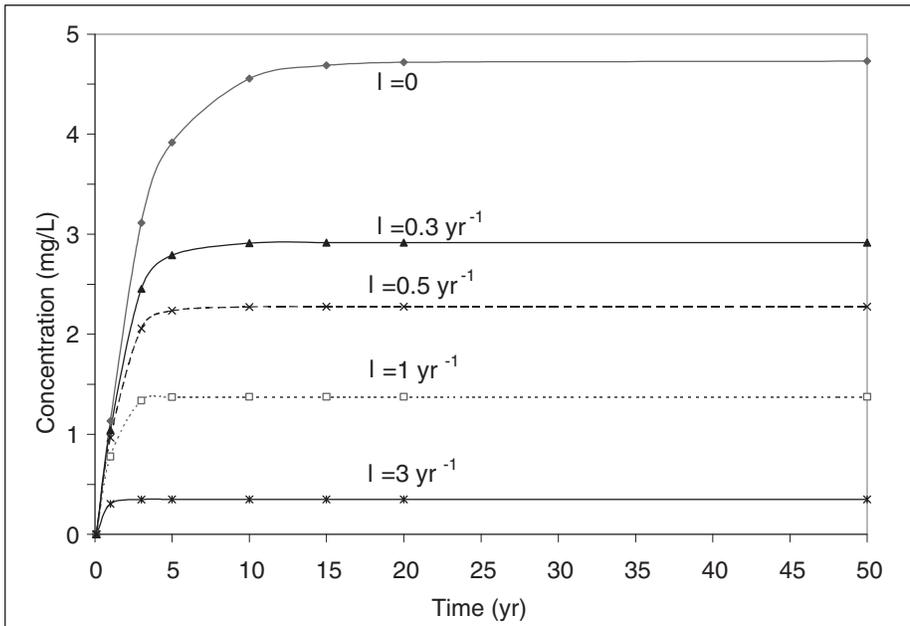
Downgradient location

Effect of Source Decay (k_{source}) on Concentration vs. Time Profiles

The figures below show concentration vs. time profiles for various source decay rates for both the source and downgradient locations. This scenario was run using the Bioscreen model (Newell et al., 1996) assuming a longitudinal dispersivity of 100 ft, no sorption and no biodegradation. The maximum concentration is shown to be inversely proportional to the source decay rate. (Note the two graphs have different scales.)

Near source location

Downgradient location

24
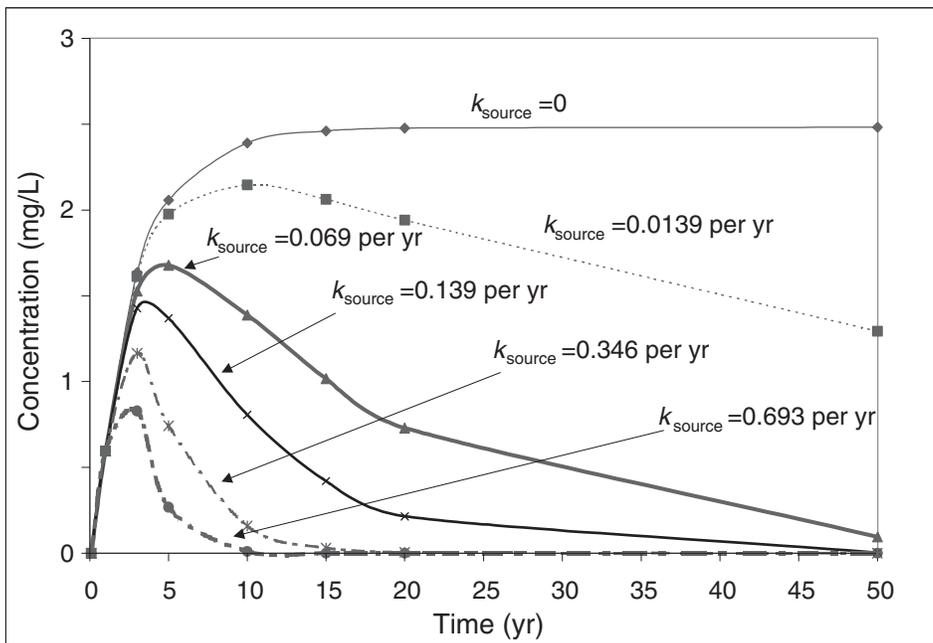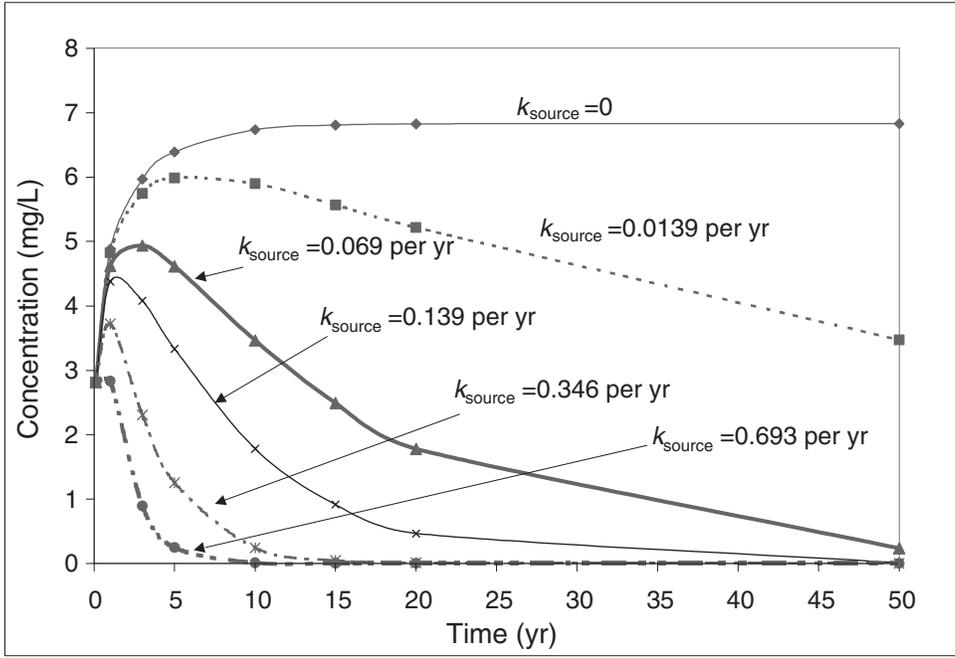
Point Attenuation Rate k_{point} as a Function of Source Decay (k_{source})

A further analysis of Concentration vs. Time profiles for different source decay rates was conducted to calculate k_{point} values. The effect of source decay on the point attenuation rate was then evaluated by plotting the calculated k_{point} as a function of k_{source} as illustrated in the figure below. This example illustrates that the point attenuation rate is proportional to the source decay rate.
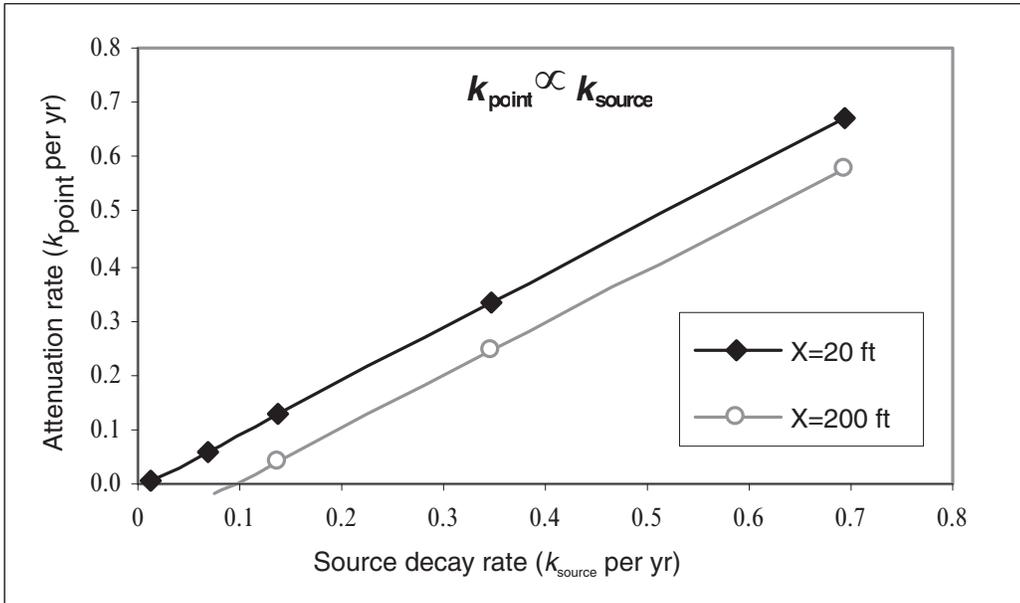
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APPENDIX A.2.   TIER 2: BOX MODEL SUMMARY

Appendix A.2.1.   Derivation of Mass and Flux-Based Source Decay Rate Constant

Purpose:
Determine the source decay rate constant relationship used in SourceDK. Note: This derivation was originally presented by Newell, et. al. (1996).

Given:
1.   There is a finite amount of soluble organic constituents in the source zone box (in the dissolved, sorbed, and NAPL phases.

Assumptions:
1.   Source is represented as a box model.
2.   Groundwater flowrate is constant, $Q(t) = Q$
3.   The dissolved concentration vs. time relationship in the box can be approximated using a first order decay relationship:

$$C(t) = C_{gwo} e^{-k_s t}$$

where C(t) is the groundwater concentration at time t; C_{gwo} is the groundwater concentration at time 0; and k_s is the source decay constant (see Appendix A.1 for more information about decay constants). (Note: other shapes for the source concentration vs. time curve could have been selected, such as a step function or linear decay. Based on the author's experience, the first order decay assumption is a reasonable way to model the source concentration vs. time relationship).

4.   The dissolved phase concentration is directly proportional to the total mass in the box at all times resulting in the expression.

$$\frac{M(t)}{M_0} = \frac{C(t)}{C_{gwo}}$$

Calculations:
The total mass leaving the box can be expressed by integrating the concentration vs. time:

$$M_0 = Q \int_0^\infty C(t)$$

$$\frac{M_0}{Q} = \int_0^\infty C_{gwo} e^{-k_s t}$$

$$\frac{M_0}{Q C_{gwo}} = \frac{e^{-k_s \infty}}{-k_s} - \frac{e^{-k_s \cdot 0}}{-k_s}$$

$$\frac{M_0}{Q\ C_{gwo}} = \frac{e^{-k_s \cdot 0}}{k_s}$$

$$\frac{M_0}{Q\ C_{gwo}} = \frac{1}{k_s}$$

$$k_s = \frac{QC_{gwo}}{M_o}$$

Summary:

The flux-based source decay constant can be expressed as:

$$k_s = \frac{QC_{gwo}}{M_o}$$

Appendix A.2.2. Derivation of SourceDK Source Decay Relationship Incorporating Biodegradation of Dissolved Constituents in the Box Model

Purpose:
Modify the source decay relationship derived in Appendix A.2.1 to include the effects of biodegradation of dissolved constituents in the control volume (box). Use two methods to account for source mass that is lost due biodegradation in the box model: 1) enter a biodegradation rate constant (λ) for any dissolved constituent that biodegrades; and 2) enter the biodegradation capacity (use only for fuel sites and the BTEX constituents). SourceDK assumes that all the biodegradation takes place in the dissolved phase and only acts on dissolved constituent in the box (the control volume).

Given:
1. Decay starts at time t = 0.
2. There is a finite amount of soluble constituent in the source zone box in the dissolved, sorbed, or NAPL phases (M_o).

Procedure:
1. Determine the rate of constituent removal from the source box.
2. Apply initial conditions for concentration at time = 0 and solve for concentration.

Assumptions:
1. Source is a represented as a box model.
2. Groundwater flowrate is constant, Q(t) = Q
3. Change in concentration can be approximated as a first order reaction.

Calculations:
1. For petroleum solvent sites, the rate of constituent discharge from the box can be represented as the sum of removal through mass discharge and removal through biodegradation

$$r_{Dis} = k_S C + k_{SB} C \qquad (1)$$

where

r_{Dis} = rate of constituent removal from box

k_s = decay coefficient of source due to mass discharge from box

C = concentration

k_{SB} = decay coefficient due to biodegradation of dissolved constituents in box

2. Rate of constituent removal is the rate of change of concentration over time

$$-\frac{dC}{dt} = k_S C + k_{SB} C \qquad (2)$$

3. Factoring terms in Equation 2

$$-\frac{dC}{dt} = (k_S + k_{SB})C \qquad (3)$$

4.   Rearranging Equation 3

$$-\frac{dC}{C} = \left(k_S + k_{SB}\right)dt \qquad (4)$$

5.   Integrating Equation 4 over time to determine the concentration at time t

$$-\int_{C_{gwo}}^{C_t} \frac{dC}{C} = \int_0^t \left(k_S + k_{SB}\right)dt \qquad (5)$$

$$-\ln\left(\frac{C_t}{C_{gwo}}\right) = \left(ks + k_{SB}\right)t \qquad (6)$$

$$C_t = C_{gwo} \exp\left\{-\left(ks + k_{SB}\right)t\right\} \qquad (7)$$

6.   Substituting the equation for rate of decay through mass discharge only (the decay coefficient derived in Appendix A.2.1)

$$C_t = C_{gwo} \exp\left\{-\left(\frac{QC_{gwo}}{M_o} + k_{SB}\right)t\right\} \qquad (8)$$

7.   For any site the total mass in the box is given by:

$$C_t = \frac{C_{gwo} \times M}{M_o} \qquad (9)$$

where M is the constituent mass at time t and M_o the initial constituent mass in the box.

8.   Rearranging Equation 11 yields:

$$M = \frac{C_t \times M_o}{C_{gwo}} \qquad (10)$$

9.   A mass balance on the mass in the box gives:

$$\frac{dM}{dt} = \frac{M_o}{C_{gwo}} \frac{dC_t}{dt} = QC_{gwi} - QC_t - \lambda C_t \phi V \qquad (11)$$

where:

Q = flow rate through the box (ft^3/yr)
C_{gwi} = concentration of constituent entering the box (mg/L)
λ = first-order decay coefficient (1/yr)

Φ = porosity (-)

V = volume of the box (ft^3).

10. Rearranging Equation 13 and recognizing that $C_{gwi} = 0$

$$\frac{dC_t}{C_t} = -\frac{C_{gwo}}{M_o}(Q + \lambda\phi V)dt \qquad (12)$$

11. Solving Equation 14 yields

$$C_t = C_{gwo}\exp\left\{-\left(\frac{C_{gwo}}{M_o}(Q + \lambda\phi V)\right)t\right\} \qquad (13)$$

12. Accounting for any additional source decay as a percentage of advective flux, Equation 15 becomes

$$C_t = C_{gwo}\exp\left\{-\left(\frac{Q + \lambda\phi V}{M_o}\right)C_{gwo}t\right\} \qquad (14)$$

13. For hydrocarbon fuel sites being modeled using biodegradation capacity, the rate of decay through biodegradation equals:

$$k_{SB} = \frac{Q \times BC \times \dfrac{PercentBC}{100}}{M_o} \qquad (15)$$

where BC is the biodegradation capacity that accounts for biological reactions that occur until the available electron acceptors in the groundwater are consumed, and PercentBC is the percent biodegradation capacity applied to constituent.

14. Therefore, the concentration at any time t ≥ 0 for the petroleum hydrocarbon sites in SourceDK is:

$$C_t = C_{gwo}\exp\left(-\frac{Q\left(C_{gwo} + BC \times \dfrac{PercentBC}{100}\right)}{M_o}t\right) \qquad (16)$$

Summary:

For any site where biodegradation of constituents in the control volume can be expressed with a first order decay relationship and a biodegradation rate constant (λ), the concentration at any time $t \geq 0$ in SourceDK is:

$$C_t = C_{gwo} \exp\left\{-\left(\frac{Q + \lambda \phi V}{M_o}\right) C_{gwo} t\right\}$$

For hydrocarbon fuel sites being modeled using biodegradation capacity, the concentration at any time $t \geq 0$ in SourceDK can also be expressed with the following relationship using:

$$C_t = C_{gwo} \exp\left(-\frac{Q(C_{gwo} + BC \times \frac{PercentBC}{100})}{M_o} t\right)$$

Appendix A.2.3. Derivation of SourceDK First-Order Delayed Decay Concentration

Purpose:
Determine the first-order delayed decay source concentration relationship used in SourceDK.

Given:
1.   There is a delay in time before decay starts, that is decay starts at time t = t_{trig}.

Procedure:
1.   Determine the condition for delayed decay.
2.   Calculate initial mass of constituents in the box (total constituents in the dissolved, sorbed, and NAPL phases), M_o.
3.   Determine the mass of constituents at the time when decay starts, M_{trig}.
4.   Determine the concentration of constituents in groundwater when decay starts.
5.   Apply decay conditions at time t = t_{trig} into expressions for concentration at time t ≥ 0.

Assumptions:
1.   Source is a represented as a box model.
2.   Groundwater flowrate is constant, Q(t) = Q
3.   Change in concentration can be approximated as a first order reaction.

Calculations:
1.   The concentration of constituents in groundwater leaving the box at time t = t_{trig} equals the initial concentration C_{gwo}.

$$C_{t_{trig}} = C_{gwo} \qquad (1)$$

2.   The mass of constituents, M_{trig}, leaving the box at time t = t_{trig} is given by

$$M_{trig} = M_o - QC_{gwo}t_{trig} \qquad (2)$$

where

   M_{trig} = mass in the source box at time t = t_{trig} (kg)
   M_o = mass of constituents at time t=0 (kg)
   Q = flow of groundwater through the box (ft^3/yr)
   C_{gwo} = concentration of constituents in groundwater at time t = t_{trig} (mg/L)

3.   For petroleum fuel sites, the concentration of organic compounds leaving the box after time t ≥ 0 without delayed decay is given by Equation 10 of Appendix A.2.2

$$C_t = C_{gwo} \exp\left\{-\left(\frac{Q(C_{gwo} + BC \times \frac{PercentBC}{100})}{M_o}\right)t\right\} \qquad (3)$$

4.   At time t = t_{trig}, the mass of constituents in the source zone decrease to M_{trig}.

$$C_{trig} = C_{gwo} \exp\left\{-\left(\frac{Q\ (C_{gwo} + BC \times \frac{PercentBC}{100})}{M_{trig}}\right)t_{trig}\right\} \qquad (4)$$

Substituting Equation 2 into Equation 4:

$$C_{trig} = C_{gwo} \exp\left\{-\left(\frac{Q(C_{gwo} + BC \times \frac{PercentBC}{100})}{M_o - QC_{gwo}t_{trig}}\right)t_{trig}\right\} \qquad (5)$$

5. Accounting for the delay in time, the concentration of constituents at time $t \geq t_{trig}$ at petroleum fuel sites can be represented as

$$C_t = C_{gwo} \exp\left\{-\left(\frac{Q(C_{gwo} + BC \times \frac{PercentBC}{100})}{M_o - QC_{gwo}t_{trig}}\right)(t - t_{trig})\right\} \qquad (6)$$

6. Similarly for sites where biodegradation is represented by a first order decay rate constant (λ), the concentration of constituents at time $t \geq t_{trig}$ can be represented as

$$C_t = C_{gwo} \exp\left\{-\left(\frac{(Q + \lambda\phi V)C_{gwo}}{M_o - QC_{gwo}t_{trig}}\right)(t - t_{trig})\right\} \qquad (7)$$

7. Rearranging Equation 6 solving for time for petroleum fuel sites yields:

$$t = \left\{-\left(\frac{M_o - QC_{gwo}t_{trig}}{Q(C_{gwo} + BC \times \frac{PercentBC}{100})}\right)\ln\left(\frac{C_t}{C_{gwo}}\right)\right\} + t_{trig} \qquad (8)$$

while rearranging Equation 7 for biodegradation with λ sites yields:

$$t = \left\{-\left(\frac{M_o - QC_{gwo}t_{trig}}{(Q + \lambda\phi V)C_{gwo}}\right)\ln\left(\frac{C_t}{C_{gwo}}\right)\right\} + t_{trig} \qquad (9)$$

Summary:
For any site where biodegradation of dissolved-phase constituents in the control volume can be expressed with a first order decay relationship and a biodegradation rate constant (λ), the dissolved phase concentration of the constituent at time $t \geq t_{trig}$ is given by

$$C_t = C_{gwo} \exp\left\{-\left(\frac{(Q + \lambda\phi V)C_{gwo}}{M_o - QC_{gwo}t_{trig}}\right)(t - t_{trig})\right\}$$

Note when $t_{trig} = 0$ the equation reduces to Equation 15 of Appendix A.2.2. The time required to achieve a given concentration is obtained from

$$t = \left\{-\left(\frac{M_o - QC_{gwo}t_{trig}}{(Q + \lambda\phi V)C_{gwo}}\right)\ln\left(\frac{C_t}{C_{gwo}}\right)\right\} + t_{trig}$$

For petroleum fuel sites being modeled using biodegradation capacity, the concentration of the dissolved constituent at time $t \geq t_{trig}$ can also be expressed using:

$$C_t = C_{gwo} \exp\left\{-\left(\frac{Q(C_{gwo} + BC \times \frac{PercentBC}{100})}{M_o - QC_{gwo}t_{trig}}\right)(t - t_{trig})\right\}$$

Note when $t_{trig} = 0$ the equation reduces to Equation 10 of Appendix A.2.2. The time required to achieve a given concentration is obtained from

$$t = \left\{-\left(\frac{M_o - QC_{gwo}t_{trig}}{Q(C_{gwo} + BC \times \frac{PercentBC}{100})}\right)\ln\left(\frac{C_t}{C_{gwo}}\right)\right\} + t_{trig}$$

Appendix A.2.4.   Derivation of SourceDK Mass

Purpose:
Determine the mass relationship used in SourceDK Tier 2 Box Model.

Given:
1.   There is a delay in time before decay starts.

Procedure:
1.   Calculate initial mass of constituents in the box (total constituents in the dissolved, sorbed, and NAPL phases), M_o.
2.   Determine the mass of dissolvable organics at the time when decay starts, M_{trig}.
3.   Determine the concentration of dissolvable organics in groundwater when decay starts.
4.   Apply decay conditions at time t = t_{trig} to expressions for concentration at time t ≥ 0.

Assumptions:
1.   Source is a represented as a box model.
2.   Groundwater flowrate is constant, $Q(t) = Q_o$
3.   Change in concentration can be approximated as a first order reaction.

Calculations:
1.   Calculate initial mass of dissolved/soluble organic compound, M_o.

2.   The dissolved concentration of the constituent in groundwater is directly related to the total mass of the constituent in the box at all times.

$$C_t = \frac{M_t}{V} \qquad (1)$$

3.   The ratio of concentrations at time = t to the concentration at time = 0 yields

$$\frac{C_t = \dfrac{M_t}{V}}{C_o = \dfrac{M_o}{V}} \qquad (2)$$

4.   Rearranging terms in Equation 2

$$\frac{C_t}{C_o} = \frac{M_t}{M_o} \qquad (3)$$

$$M_t = M_{trig}\,\frac{C_t}{C_o} \qquad (4)$$

5.   At time t = t_{trig}, $C_{gwo} = C_{t_{trig}}$, and

$$M_o = M_{trig} = M_o - QC_{gwo}t_{trig} \qquad (5)$$

6.   Substituting terms in Equation 4

$$M_t = \left(M_o - QC_{gwo}t_{trig}\right)\frac{C_t}{C_{gwo}} \qquad (6)$$

7.   For petroleum fuel sites with a BTEX constituent, the mass of constituent at any time t, is obtained by substituting C_t of Equation 6 by Equation 6 of Appendix A.2.3

$$M_t = \left(M_o - QC_{gwo}t_{trig}\right)\frac{C_{gwo}\,\exp\left\{-\left(\frac{Q_o\left(C_{gwo} + BC\times\frac{PercentBC}{100}\right)}{M_o - QC_{gwo}t_{trig}}\right)(t - t_{trig})\right\}}{C_{gwo}} \qquad (7)$$

8.   Simplifying terms

$$M_t = \left(M_o - QC_{gwo}t_{trig}\right)\exp\left\{-\left(\frac{Q_o\left(C_{gwo} + BC\times\frac{PercentBC}{100}\right)}{M_o - QC_{gwo}t_{trig}}\right)(t - t_{trig})\right\} \qquad (8)$$

9.   For any site where biodegradation of dissolved constituents in the control volume can be expressed with a first order decay relationship and a biodegradation rate constant (λ), mass of the constituents at any time is obtained by substituting C_t of Equation 6 above by Equation 7 of Appendix A.2.3

$$M_t = \left(M_o - QC_{gwo}t_{trig}\right)\frac{C_{gwo}\,\exp\left\{-\left(\frac{(Q_o + \lambda\phi V)C_{gwo}}{M_o - QC_{gwo}t_{trig}}\right)(t - t_{trig})\right\}}{C_{gwo}} \qquad (9)$$

10.   Simplifying terms

$$M_t = \left(M_o - QC_{gwo}t_{trig}\right)\exp\left\{-\left(\frac{(Q_o + \lambda\phi V)C_{gwo}}{M_o - QC_{gwo}t_{trig}}\right)(t - t_{trig})\right\} \qquad (10)$$

Summary:
The mass at any time t ≥ 0 for any site where biodegradation of dissolved constituents in the control volume can be expressed with a first order decay relationship and a biodegradation rate constant (λ) can be obtained from:

$$M_t = \left(M_o - QC_{gwo}t_{trig}\right)\exp\left\{-\left(\frac{(Q_o + \lambda\phi V)C_{gwo}}{M_o - QC_{gwo}t_{trig}}\right)(t - t_{trig})\right\}$$

The mass at any time t ≥ 0 for petroleum fuel sites being modeled using biodegradation capacity can be obtained from

$$M_t = \left(M_o - QC_{gwo}t_{trig}\right)\exp\left\{-\left(\frac{Q_o(C_{gwo} + BC \times \dfrac{PercentBC}{100})}{M_o - QC_{gwo}t_{trig}}\right)(t - t_{trig})\right\}$$

APPENDIX A.3. BIODEGRADATION CAPACITY CALCULATION (FROM NEWELL *ET AL*., 1996)

To apply the biodegradation first-order decay model, the amount of biodegradation able to be supported by the groundwater that moves through the source zone must be calculated. The conceptual model used in SourceDK is:

1. Groundwater upgradient of the source contains electron acceptors.

2. As the upgradient groundwater moves through the source zone, non-aqueous phase liquids (NAPLs) and contaminated soil release dissolvable hydrocarbons (in the case of petroleum sites, the BTEX compounds benzene, toluene, ethylbenzene, and xylene are released).

3. Biological reactions occur until the available electron acceptors in groundwater are consumed. (Two exceptions to this conceptual model are the iron reactions, where the electron acceptor, ferric iron, dissolves from the aquifer matrix; and the methane reactions, where the electron acceptor, CO_2 is also produced as an end product of the reactions. For these reactions, the metabolic by-products, ferrous iron and methane, can be used as proxies for the potential amount of biodegradation that could occur from the iron-reducing and methanogenesis reactions.)

4. The total amount of available electron acceptors for biological reactions can be estimated by a) calculating the difference between upgradient concentrations and source zone concentrations for oxygen, nitrate, and sulfate; and b) measuring the production of metabolic by-products (ferrous iron and methane) in the source zone.

5. Using stoichiometry, a utilization factor can be developed showing the ratio of the oxygen, nitrate, and sulfate consumed to the mass of dissolved hydrocarbon degraded in the biodegradation reactions. Similarly, utilization factors can be developed to show the ratio of the mass of metabolic by-products that are generated to the mass of dissolved hydrocarbon degraded in the biodegradation reactions. Wiedemeier, *et al*., (1995) provides the following utilization factors based on the degradation of combined BTEX constituents:

Electron Acceptor/By-Product	BTEX Utilization Factor gm/gm
Oxygen	3.14
Nitrate	4.9
Ferrous Iron	21.8
Sulfate	4.7
Methane	0.78

6. For a given background concentration of an individual electron acceptor, the potential constituent mass removal or "biodegradation capacity" depends on the "utilization factor" for that electron acceptor. Dividing the background concentration of an electron acceptor by its utilization factor provides an estimate (in BTEX concentration units) of the assimilative capacity of the aquifer by that mode of biodegradation.

Note that SourceDK is based on the BTEX utilization provided above. If other constituents are modeled, the utilization factors in the software (scroll down from the input screen to find the utilization factors) should be changed or the available oxygen,

nitrate, iron, sulfate, and methane data should be adjusted accordingly to reflect alternate utilization factors.

When the available electron acceptor/by-product concentrations (No. 4) are divided by the appropriate utilization factor (No. 5), an estimate of the "biodegradation capacity" of the groundwater flowing through the source zone and plume can be developed. The biodegradation capacity is then used directly in the SourceDK model to simulate the effects of an instantaneous reaction. The suggested calculation approach to develop SourceDK input data is:

Biodegradation Capacity (mg/L) =

{(Average Upgradient Oxygen Conc.) - (Minimum Source Zone Oxygen Conc)} / 3.14
+{(Average Upgradient Nitrate Conc.) - (Minimum Source Zone Nitrate Conc)} /4.9
+{(Average Upgradient Sulfate Conc.) - (Minimum Source Zone Sulfate Conc)} / 4.7
+{Average Observed Ferrous Iron Conc. in Source Area} / 21.8
+{Average Observed Methane Conc. in Source Area} / 0.78

Biodegradation capacity is similar to "expressed assimilative capacity" described in the AFCEE Technical Protocol, except that expressed assimilative capacity is based on the maximum observed concentration observed in the source zone for iron and methane, while the biodegradation capacity term used in SourceDK is based on the average concentration in the source zone for iron and methane. SourceDK uses the more conservative biodegradation capacity approach to provide a conservative screening tool to users. Calculated biodegradation capacities (from Groundwater Services sites) and expressed assimilative capacities (from Parsons Engineering-Science sites) at different U.S. Air Force RNA research sites have ranged from 7 to 70 mg/L. The median capacity for 28 AFCEE sites is 28.5 mg/L.

SourceDK assumes that all of the biodegradation reactions (aerobic and anaerobic) occur almost instantaneously relative to the hydraulic residence time in the source area and plume. Because iron reduction and methane production appear to occur only in the source zone (probably due to the removal of these metabolic by-products) it is recommended to use the average iron and methane concentrations observed in the source zone for the calculation of biodegradation capacity instead of maximum concentrations. In addition, the iron and methane concentrations are used during a secondary calibration step (see below). Application of the biodegradation capacity approach indicated that the use of the maximum concentration of iron and methane tended to overpredict biodegradation at many sites by assuming these reactions occurred over the entire plume area. Use of an average value (or some reduced value) helps match actual field data.

7. Note that at some sites the model will appear to overpredict the amount of biodegradation that occurs, and underpredict at others. As is the case of the first-order decay models, some calibration to actual site conditions is required. The following procedure is recommended:

> Reevaluate the biodegradation capacity calculation. There is some judgment involved in averaging the electron acceptor concentrations observed in upgradient wells; determining the minimum oxygen, nitrate and sulfate in the source zone; and estimating the average ferrous iron and methane concentrations in the source zone. Although probably not needed in most applications, these values may be adjusted as a final level of calibration.

APPENDIX A.4.   TIER 3: PROCESS MODELS SUMMARY

Appendix A.4.1.   Tier 3 Dissolved-Phase Only Process Model

Purpose:
Determine the time and pore volume relationship for Tier 3 dissolved phase model in SourceDK.

Given:
1.   There is a finite amount of soluble constituents in the source zone.
2.   These constituents are flushed slowly from the control volume as fresh groundwater passes though.

Procedure:
1.   Determine the ratio of the original concentration to the desired cleanup level.
2.   Calculate the number of pore volumes required to flush out dissolved constituents.
3.   Account for retardation by multiplying number of pore volumes by retardation factor.
4.   Calculate the time required to achieve the required pore volume flush and reach desired cleanup levels.

Assumptions:
1.   There is no NAPL present.
2.   Groundwater flow rate is constant, $Q(t) = Q_o$
3.   Groundwater flowing through the box is free of constituents. This implies that no mass is added to the system and only desorption of dissolved constituents occurs.
4.   The aquifer is homogeneous.
5.   There is no biodegradation occurring.

Calculations:
1.   For dissolved phase constituents, pore volumes are calculated based on the simple flushing model developed by Newell *et al*. (1994). This model is based on the one-dimensional advection-dispersion equation presented by Ogata and Banks (1961)

$$\frac{C_t}{C_o} = \frac{1}{2} erfc\left(\frac{L - v_x t}{2\sqrt{\alpha_x v_x t}}\right) \qquad (1)$$

where

C_t = concentration at any time t at any distance L along the control volume (mg/L)
C_o = original concentration at time t = 0 at any point within the control volume (mg/L)
L   = length along flow path in control volume parallel to the groundwater flow (ft)
v_x = groundwater seepage velocity (ft/yr)
t   = time (yr)
α_x = longitudinal dispersivity (ft)

2.   The number of pore volumes that pass through a control volume during a certain time t is

$$PV = \frac{v_x t}{L} \qquad (2)$$

where

PV = pore volumes (unitless)
v_x = groundwater seepage velocity (ft/yr)
t = time (yr)
L = length along flow path in control volume parallel to the groundwater flow (ft)

3. Rearranging Equation 2

$$L = \frac{v_x t}{PV} \qquad (3)$$

4. Applying the common assumption that the longitudinal dispersivity is equal to 10% of length (see ASTM, 1995; Newell *et al.*, 1996), Equation 1 becomes

$$\frac{C_t}{C_o} = \frac{1}{2} erfc\left(\frac{L - v_x t}{2\sqrt{0.1 L v_x t}}\right) \qquad (4)$$

5. Substituting for *L* in Equation 3

$$\frac{C_t}{C_o} = \frac{1}{2} erfc\left(\frac{\left(v_x t / PV\right) - v_x t}{2\sqrt{0.1\left(v_x t / PV\right) v_x t}}\right) \qquad (5)$$

which reduces to

$$\frac{C_t}{C_o} = \frac{1}{2} erfc\left(1.58\left[\frac{\left(1/PV\right) - 1}{\sqrt{1/PV}}\right]\right) \qquad (6)$$

6. Although Equation 6 cannot be solved directly for pore volumes, it can be depicted graphically as PV as a function of C_t/C_o. This resulting graph (see Figure A.4-1) is almost linear throughout the region of interest ($C_t/C_o < 0.1$), and yields the following approximation

$$PV = -0.93 \log_{10} \frac{C_t}{C_o} + 0.75 \qquad (7)$$

7. Even though this approximation does not account for retardation, the number of pore volumes can be adjusted to account for retardation by multiplying *PV* by the appropriate retardation factor *R*.

Appendix A.4.2.   Tier 3 NAPL Dissolution Model

Purpose:
Determine the time and pore volume relationship for Tier 3 NAPL dissolution model in SourceDK.

Given:
1.   There is a finite amount of a single-component NAPL compound in the source zone.
2.   The NAPL dissolves slowly as fresh groundwater passes though the source zone.

Procedure:
1.   Determine the ratio of the original concentration to the desired cleanup level.
2.   Calculate the number of pore volumes required to dissolve the NAPL.
3.   Calculate the time required to achieve the required pore volume flush and reach desired cleanup levels.

Assumptions:
1.   The NAPL is present as a single-component NAPL.
2.   Groundwater flow rate is constant, $Q(t) = Q_o$
3.   Groundwater flowing into the upstream face of the box is free of constituents. This implies that no mass is added to the system and only dissolution of the NAPL occurs.
4.   The aquifer is homogeneous.
5.   There is no biodegradation occurring.
6.   The effect of dispersion can be neglected.

Calculations:
1.   For NAPL-affected source zones, pore volumes are determined from the theta model originally developed by Powers *et al*. (1994) and modified in Newell *et al*. (1994)

$$PV = \frac{\rho \times 10^6}{\alpha C_s} S_o \qquad (1)$$

where

ρ = NAPL density (g/ml)
So = initial NAPL saturation (fraction of pore space)
Cs = the initial aqueous phase concentration under natural flow conditions (mg/L)
α   = empirical measure of the effects of soil permeability and uniformity index (read off Fig 2.32 of "Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface" by Wiedemeier *et al*., 1999 see Figure A.4-2 below) (unitless)

2.   To account for any additional pumping and source decay as part of advective flux, Equation 1 becomes

$$\frac{\rho \dfrac{S_o}{100} 10^6}{\left(C_s \, or \, C_{s_{pumping}}\right)\alpha} \qquad (2)$$

Where

$$C_{s_{pumping}} = C_s \sqrt{\frac{V_x}{V_{pumping}}}$$ (see Appendix A.4.3)

where

ρ = NAPL density (g/ml)
S_o = initial NAPL saturation (fraction of pore space)
C_s = initial aqueous phase concentration under natural flow conditions (mg/L)
$C_{spumping}$ = concentration in produced groundwater as a result of mass transfer effects (use if groundwater velocities are artificially high due to pumping) (mg/L)
α = empirical measure of the effects of soil permeability and uniformity index. Read off Fig 2.32 of "Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface" by Wiedemeier *et al*., 1999 (unitless)
V_x = natural groundwater seepage velocity (ft/yr)
$V_{pumping}$ = typical groundwater seepage velocity while pumping (use if groundwater velocities are artificially high due to pumping) (ft/yr)

3.   Once the number of pore values has been estimated, the time taken under natural attenuation for groundwater flow to flush out dissolved constituents and reach desired cleanup levels can be determined by

$$t = \frac{PV \times L}{v_x}$$ (3)

Summary:
For **dissolved phase only control volumes**, the number of pore volumes required to reach the desired cleanup level can be calculated from

$$PV = -0.93 \log_{10} \frac{C_t}{C_o} + 0.75$$ for C_t/C_o < 0.1

The number of pore volumes accounting for retardation is given by

$$PV = PV \times R$$

For dissolved phase only, the pore volumes can be obtained from Figure A.4-1.

For **control volumes containing NAPL**, the number of pore volumes required to reach the desired cleanup level can be calculated from

$$PV = \frac{\rho \frac{S_o}{100} 10^6}{\left(C_s \, or \, C_{s_{pumping}}\right)\alpha}$$

Pore volumes for NAPL phase constituents can be obtained from Figure A.4-2.

The time required for natural attenuation to flush out dissolved constituents and achieve desired cleanup levels is determined by

$$t = \frac{PV \times L}{v_x}$$
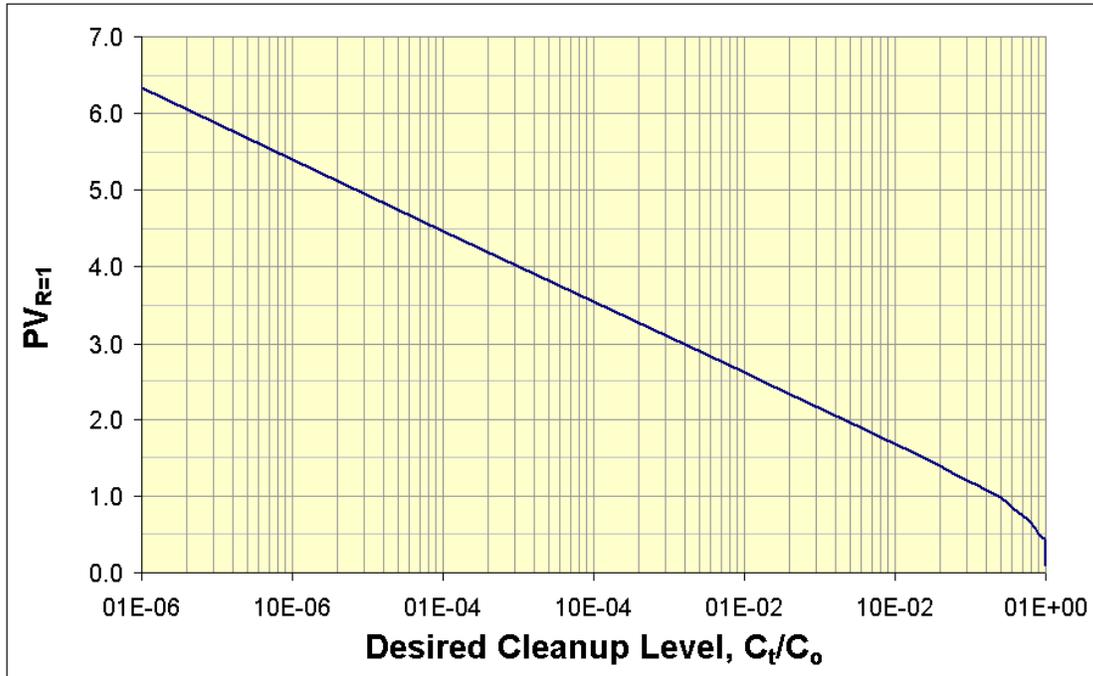
Figure A.4-1. Pore volumes required to flush dissolved-phase constituents from porous media assuming no retardation (R=1) and no NAPL. To account for retardation, multiply pore volumes by the calculated retardation factor. (From Newell *et al*., 1994.)
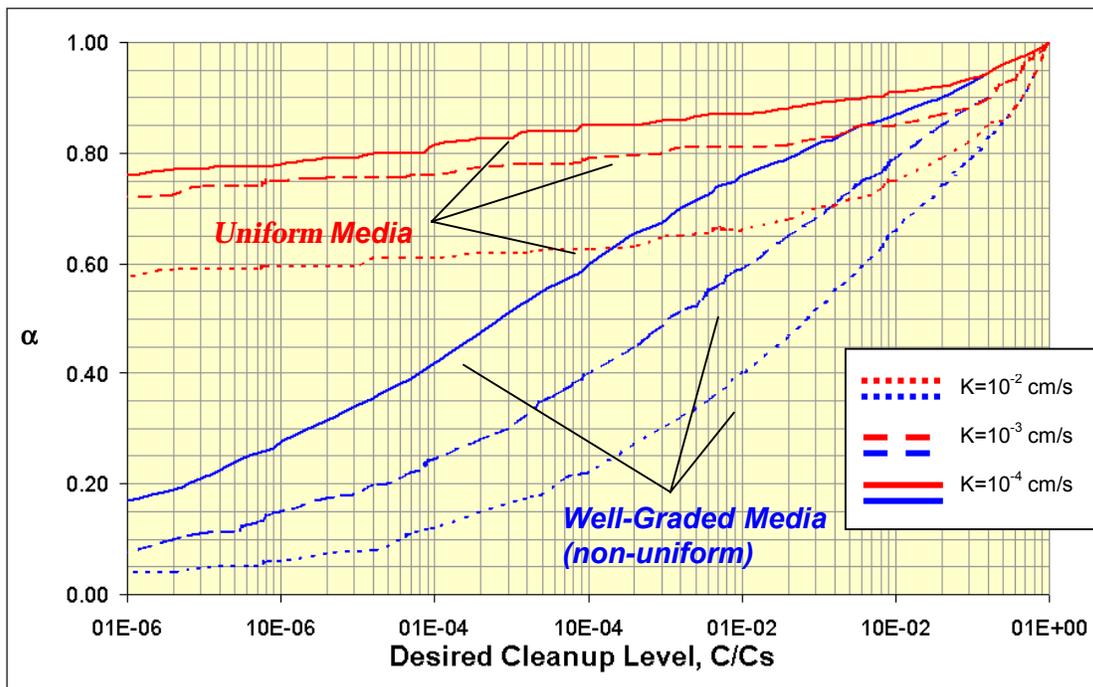
Figure A.4-2.   Pore volumes required to flush aqueous-phase constituents from single component residual NAPL in homogeneous soils. α is a solubility scaling coefficient to account for decreasing NAPL solubility as water is flushed through the aquifer (Newell *et al*., 1994, Powers *et al*., 1994) and depends on porous media properties.   Curves are based on simplification of the theta model developed by Powers *et al*. (1994) (From Newell *et al*., 1994.)

Appendix A.4.3. Accounting for Mass Transfer Effects from Pump-and-Treat Systems

Several analyses have been performed to evaluate the effect of increased pumping rates on the DNAPL dissolution rate for both fingers and pools. In a paper written by Hunt *et al.* in 1988, the authors developed relationships for the kinetics of dissolution in NAPL source zones. They evaluated laboratory studies and mass transfer approaches used in the chemical engineering literature, and derived dissolution expressions for residual NAPL ganglia (also called "fingers" or "blobs"). They concluded that:

"Ganglion lifetimes are weakly dependent on flow velocity such that to decrease the lifetime from 100 years to 10 years requires a three order of magnitude increase (x1000) in flow velocity."

In other words, increasing the groundwater pumping rate will increase the finger dissolution rate, but based on Hunt *et al.*'s description will follow this approximation:

$$\frac{\text{mass transfer rate with pumping}}{\text{mass transfer rate without pumping}} = 10^{\dfrac{\log 10\left[\dfrac{Q_{\text{pumping}}}{Q_{\text{natural}}}\right]}{3}} \qquad (1)$$

Using this NAPL dissolution relationships reported by Hunt *et al.* (1988), a pumping system that increases the natural flow rate through the system by a factor of 10 (for example, from 100 gpm to 1000 gpm) would result in a net increase in mass removed only by a factor of 2.1 due to reduced concentrations caused by mass transfer effects):

$$\frac{\text{mass transfer rate with pumping}}{\text{mass transfer rate without pumping}} = 10^{\dfrac{\log 10\left[\dfrac{1000\,\text{gpm}}{100\,\text{gpm}}\right]}{3}} = 2.1 \qquad (2)$$

The same type of concentration reduction is expected when higher groundwater flowrates are used to dissolve NAPL pools. Dissolution kinetic relationships developed by Johnson and Pankow (1992) indicate that the mass transfer rate (and pool lifetime) changes with the square root of groundwater velocity:

$$\text{Pool Dissolution Time (yrs)} = 2.43 \times 10^{-5}\, \rho_D C_{\text{sat}}\, [\, l_p^{3}/D_v\, v_d\,]^{0.5} \qquad (3)$$

where:

ρ_D = DNAPL density (g/m^3)
C_{sat} = saturation concentration (g/m^3)
l_p = length of pool in direction of groundwater flow (m)
D_v = vertical dispersion coefficient (m^2/s)
v_d = Darcy velocity for groundwater (m/day)

Therefore, increasing the groundwater flowrate over a pool by a factor of 10 would result in an initial concentration *decrease* by a factor of 3.2 (approximately the square root of 10), and the overall *increase* in the mass removal rate by only a factor of 3.2.

These theoretical expressions appear to be supported by lab and field data that show reduced concentrations in pumping system compared to non-pumping conditions.   These simple

relationships can be used to approximate mass transfer effects of water being pumped through NAPL zones. For SourceDK, the more conservative relationship of the concentration reduction being proportional to the square root of the increase in groundwater velocity was used:

$$C_{s\,pumping} = C_s \sqrt{\frac{V_x}{V_{pumping}}} \qquad\qquad (4)$$

where

C_s = initial aqueous phase concentration under natural flow conditions (mg/L)

$C_{spumping}$ = concentration in produced groundwater as a result of mass transfer effects (use if groundwater velocities are artificially high due to pumping) (mg/L)

V_x = natural groundwater seepage velocity (ft/yr)

$V_{pumping}$ = typical groundwater seepage velocity while pumping (use if groundwater velocities are artificially high due to pumping) (ft/yr)

APPENDIX A.5.   TIER 1: EMPIRICAL DATA TREND EXTRAPOLATION MODEL CONFIDENCE LIMIT CALCULATION

Purpose:
Determine the 95 percent confidence interval of time required to achieve clean-up to a specified level.

Given:
1.   There is a finite amount of soluble organic compound in the source zone.
2.   These organics dissolve slowly as fresh groundwater passes though the source zone.

Procedure:
1.   Using a calculator or spreadsheet, plot ln(concentrations) (y-axis) versus time in years (x-axis) and obtain a best fit line through the data. Determine the slope, β and the intercept, β_o of the regression line.

2.   Find the target concentration, $\hat{Y}_{x_0}$. This is the concentration value at the target time, x_o , i.e. the natural logarithm of the clean-up level concentration value.

3.   Determine the Student t-test value, $t_{n-2,1-\alpha/2}$ using α = 0.05 (for a 95% confidence interval) and the number of samples, *n*.   This value is obtained from a table of Student's t-test values in any standard statistics book (e.g., Richard O. Gilbert, "Statistical Methods For Environmental Pollution Monitoring", 1987. Van Nostrand Reinhold Company Inc., Table A2).

4.   To calculate the quantity, $S_{y|x}$, use a calculator or a spreadsheet and
   a)   Calculate the sample variance of the y-values, S_y^2.
   b)   Calculate the sample variance of the x-values, S_x^2.
   c)   Plug in values for *n*, S_y^2, S_x^2, and $\hat{\beta}$ into Equation 2 and determine the value for $S_{y|x}$

5.   Substitute the values for $\hat{\beta}$, $t_{n-2,1-\alpha/2}$, $S_{y|x}$, S_x^2, and *n* in Equation 1.
6.   Calculate the average of the x-values, $\overline{X}$

7.   Substitute the values for $\hat{\beta}_o$, $t_{n-2,1-\alpha/2}$, $S_{y|x}$, S_x^2, $\overline{X}$, and *n* in Equation 2.
8.   Adding the two terms in Equation 1 will give the upper 95% confidence interval for the slope, while subtracting the two terms will yield the lower 95% confidence interval.
9.   Add the two terms in Equation 2 to get the upper 95% confidence interval for the intercept, and subtract the two terms to get the lower 95% confidence interval.
10.   Use Equation 5 to calculate the confidence interval for the time when the concentration reaches the clean-up level.
11.   Use Equation 6 to get the upper 95% confidence interval for the date.
12.   Use Equation 7 to get the lower 95% confidence interval for the date.

Calculations:
1.   The 95% confidence interval for the slope β is given by

$$\beta_{95CI} = \hat{\beta} \pm t_{n-2,1-\alpha/2} \frac{S_{y|x}}{\sqrt{S_x^2(n-1)}} \qquad (1)$$

where

$\hat{\beta}$ = estimated slope of regression line through data
t = Student t-test statistic
n = number of samples
α = confidence coefficient
$S_{y|x}$ = standard deviation of the data
S_x^2 = variance of the x-axis

2. The 95% confidence interval for the intercept β_o is given by

$$\beta_{O95CI} = \hat{\beta}_O \pm t_{n-2,1-\alpha/2} \frac{S_{y|x}}{\sqrt{\dfrac{1}{n} + \dfrac{\overline{X}^2}{S_x^2(n-1)}}} \qquad (2)$$

where

$\hat{\beta}_o$ = estimated intercept of regression line through data
$\overline{X}$ = average of the x-axis

3. The standard deviation in the data, $S_{y|x}$, can be computationally obtained from

$$S_{y|x} = \sqrt{\frac{(n-1)}{(n-2)}\left(S_y^2 - \hat{\beta}^2 S_x^2\right)} \qquad (3)$$

where

n = number of samples
S_y^2 = variance of y-axis values
$\hat{\beta}$ = estimated slope of regression line through data
S_x^2 = variance of the x-axis

4. The 95% confidence interval for the date when concentration levels reach the clean-up value can be obtained by plotting the data and using the relationship

$$Y = \hat{\beta}_o + \hat{\beta}x \qquad (4)$$

Taking the logarithms and rearranging terms, the time required to reach the clean-up value is obtained from

$$x = \frac{Y - \hat{\beta}_o}{\hat{\beta}} \qquad (5)$$

where,

Y = the concentration at time x plotted on a semi-log scale

$\hat{\beta}_o$ = estimated intercept of regression line through data

$\hat{\beta}$ = estimated slope of regression line through data

5. The upper 95% confidence interval for the time when concentration levels reach the clean-up value can be obtained by a) adding the two terms in Equation 1 and substituting that value for $\hat{\beta}$ in Equation 5 and b) adding the two terms in Equation 2 and substituting that value for $\hat{\beta}_o$ in Equation 5.

$$x_{upper95} = \frac{Y - \left(\hat{\beta}_o + t_{n-2,1-\alpha/2} \dfrac{S_{y|x}}{\sqrt{\dfrac{1}{n} + \dfrac{\overline{X}^2}{S_x^2(n-1)}}} \right)}{\hat{\beta} + t_{n-2,1-\alpha/2} \dfrac{S_{y|x}}{\sqrt{S_x^2(n-1)}}} \qquad (6)$$

6. The lower 95% confidence interval for the time when concentration levels reach the clean-up value can be obtained by subtracting the two terms in Equations 1 and 2 and substituting that value for $\hat{\beta}$ and $\hat{\beta}_o$ in Equation 5.

$$x_{lower95} = \frac{Y - \left(\hat{\beta}_o - t_{n-2,1-\alpha/2} \dfrac{S_{y|x}}{\sqrt{\dfrac{1}{n} + \dfrac{\overline{X}^2}{S_x^2(n-1)}}} \right)}{\hat{\beta} - t_{n-2,1-\alpha/2} \dfrac{S_{y|x}}{\sqrt{S_x^2(n-1)}}} \qquad (7)$$

Summary:
The time required to reach a given clean-up level cab be calculated from

$$x = \frac{Y - \hat{\beta}_o}{\hat{\beta}}$$

For shrinking plumes, the upper 95% confidence interval of that time is obtained from

$$
x_{upper95} = \frac{Y - \left(\hat{\beta}_o + t_{n-2,1-\alpha/2} \dfrac{S_{y|x}}{\sqrt{\dfrac{1}{n} + \dfrac{\overline{X}^2}{S_x^2(n-1)}}} \right)}{\hat{\beta} + t_{n-2,1-\alpha/2} \dfrac{S_{y|x}}{\sqrt{S_x^2(n-1)}}}
$$

While the lower 95% confidence interval of that time is obtained from

$$
x_{lower95} = \frac{Y - \left(\hat{\beta}_o - t_{n-2,1-\alpha/2} \dfrac{S_{y|x}}{\sqrt{\dfrac{1}{n} + \dfrac{\overline{X}^2}{S_x^2(n-1)}}} \right)}{\hat{\beta} - t_{n-2,1-\alpha/2} \dfrac{S_{y|x}}{\sqrt{S_x^2(n-1)}}}
$$

APPENDIX A.6.   DNAPL CHARACTERIZATION

♻ EPA
Estimating Potential for Occurrence of DNAPL at Superfund Sites

Office of Emergency and Remedial Response
Hazardous Site Control Division (OS-220W)

Quick Reference Fact Sheet

GOALS

The presence of Dense Nonaqueous Phase Liquids (DNAPL) in soils and aquifers can control the ultimate success or failure of remediation at a hazardous waste site. Because of the complex nature of DNAPL transport and fate, however, DNAPL may often be undetected by direct methods, leading to incomplete site assessments and inadequate remedial designs. Sites affected by DNAPL may require a different "paradigm," or conceptual framework, to develop effective characterization and remedial actions (2).

To help site personnel determine if DNAPL-based characterization strategies should be employed at a particular site, a guide for estimating the potential for DNAPL occurrence was developed. The approach, described in this fact sheet, requires application of two types of existing site information:

- **Historical Site Use Information**
- **Site Characterization Data**

By using available data, site decision makers can enter a system of two flowcharts and a classification matrix for estimating the potential for DNAPL occurrence at a site. If the potential for DNAPL occurrence is low, then conventional site assessment and remedial actions may be sufficient. If the potential for DNAPL is moderate or high, however, a different conceptual approach may be required to account for problems associated with DNAPL in the subsurface.

BACKGROUND

DNAPLs are separate-phase hydrocarbon liquids that are denser than water, such as chlorinated solvents (either as a single component or as mixtures of solvents), wood preservative wastes, coal tar wastes, and pesticides. Until recently, standard operating practice in a variety of industries resulted in the release of large quantities of DNAPL to the subsurface. Most DNAPLs undergo only limited degradation in the subsurface, and persist for long periods while slowly releasing soluble organic constituents to ground water through dissolution. Even with a moderate DNAPL release, dissolution may continue for hundreds of years or longer under natural conditions before all the DNAPL is dissipated and concentrations of soluble organics in ground water return to background levels.

DNAPL exists in the soil/aquifer matrix as free-phase DNAPL and residual DNAPL. When released at the surface, free-phase DNAPL moves downward through the soil matrix under the force of gravity or laterally along the surface of sloping fine-grained stratigraphic units. As the free-phase DNAPL moves, blobs or ganglia are trapped in pores and/or fractures by capillary forces (7). The amount of the trapped DNAPL, known as residual saturation, is a function of the physical properties of the DNAPL and the hydrogeologic characteristics of the soil/aquifer medium and typically ranges from 5% to 50% of total pore volume. At many sites, however, DNAPL migrates preferentially through small-scale fractures and heterogeneities in the soil, permitting the DNAPL to penetrate much deeper than would be predicted from application of typical residual saturation values (16).

Once in the subsurface, it is difficult or impossible to recover all of the trapped residual DNAPL. The conventional aquifer remediation approach, ground water pump-and-treat, usually removes only a small fraction of trapped residual DNAPL (11, 21, 26). Although many DNAPL removal technologies are currently being tested, to date there have been no field demonstrations where sufficient DNAPL has been successfully recovered from the subsurface to return the aquifer to drinking water quality. The DNAPL that remains trapped in the soil/aquifer matrix acts as a continuing source of dissolved contaminants to ground water, preventing the restoration of DNAPL-affected aquifers for many years.

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DNAPL TRANSPORT AND FATE - CONCEPTUAL APPROACHES

The major factors controlling DNAPL migration in the subsurface include the following (5):

- the volume of DNAPL released;
- the area of infiltration at the DNAPL entry point to the subsurface;
- the duration of release;
- properties of the DNAPL, such as density, viscosity, and interracial tension;
- properties of the soil/aquifer media, such as pore size and permeability;
- general stratigraphy, such as the location and topography of low-permeability units;
- micro-stratigraphic features, such as root holes, small fractures, and slickensides found in silt/clay layers.

To describe the general transport and fate properties of DNAPL in the subsurface, a series of conceptual models (24) are presented in the following figures:

Case 1: DNAPL Release to Vadose Zone Only

After release on the surface, DNAPL moves vertically downward under the force of gravity and soil capillarity. Because only a small amount of DNAPL was released, all of the mobile DNAPL is eventually trapped in pores and fractures in the unsaturated zone. Infiltration through the DNAPL zone dissolves some of the soluble organic constituents in the DNAPL, carrying organics to the water table and forming a dissolved organic plume in the aquifer. Migration of gaseous vapors can also act as a source of dissolved organics to ground water (13).

After, Waterloo Centre for Groundwater Research, 1989.
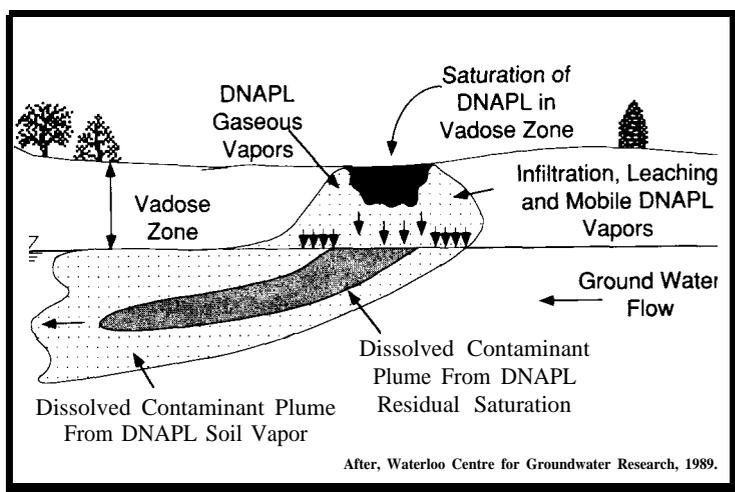
Case 2: DNAPL Release to Unsaturated and Saturated Zones

If enough DNAPL is released at the surface, it can migrate all the way through the unsaturated zone and reach a water-bearing unit. Because the specific gravity of DNAPL is greater than water, it continues downward until the mobile DNAPL is exhausted and is trapped as a residual hydrocarbon in the porous media. Ground water flowing past the trapped residual DNAPL dissolves soluble components of the DNAPL, forming a dissolved plume downgradient of the DNAPL zone. As with Case 1, water infiltrating down from the source zone also carries dissolved constituents to the aquifer and contributes further to the dissolved plume.

After, Waterloo Centre for Groundwater Research, 1989.
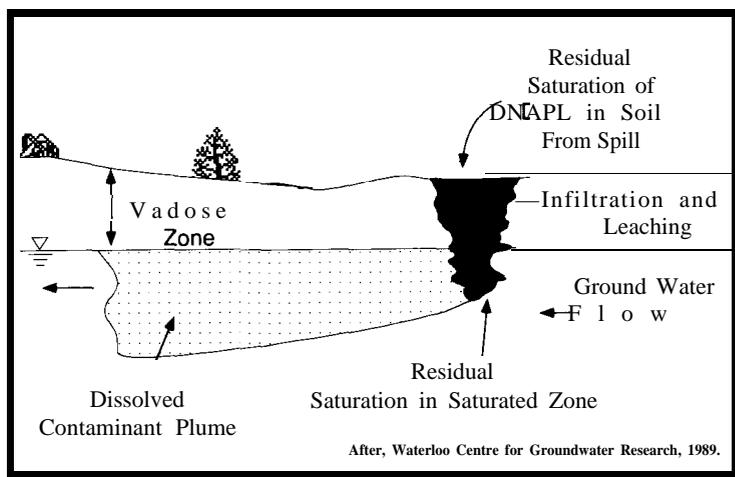
Case 3: DNAPL Pools and Effect of Low-Permeability Units

Mobile DNAPL will continue vertical migration until it is trapped as a residual hydrocarbon (Case 1 and Case 2) or until low-permeability stratigraphic units are encountered which create DNAPL "pools" in the soil/aquifer matrix. In this figure, a perched DNAPL pool fills up and then spills over the lip of the low-permeability stratigraphic unit. The spill-over point (or points) can be some distance away from the original source, greatly complicating the process of tracking the DNAPL migration.

After, Waterloo Centre for Groundwater Research, 1989.
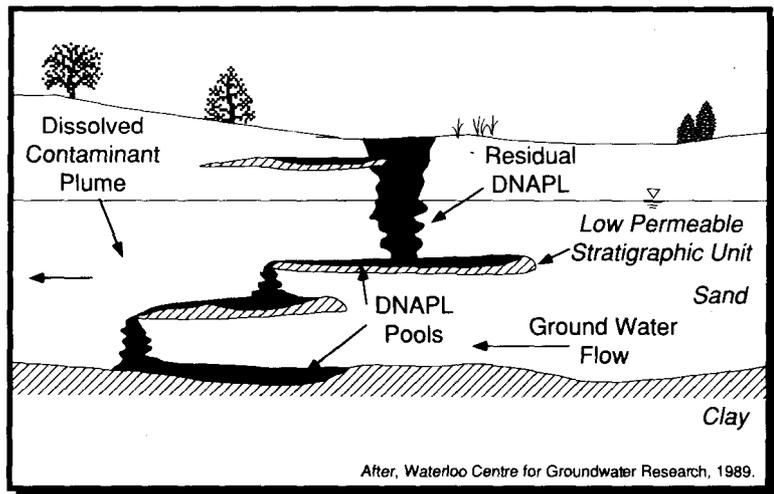
Case 4: Composite Site

In this case, mobile DNAPL migrates vertically downward through the unsaturated zone and the first saturated zone, producing a dissolved constituent plume in the upper aquifer. Although a DNAPL pool is formed on the fractured clay unit, the fractures are large enough to permit vertical migration downward to the deeper aquifer (see Case 5, below). DNAPL pools in a topographic low in the underlying impermeable unit and a second dissolved constituent plume is formed.

After, Waterloo Centre for Ground Water Research, 1989.
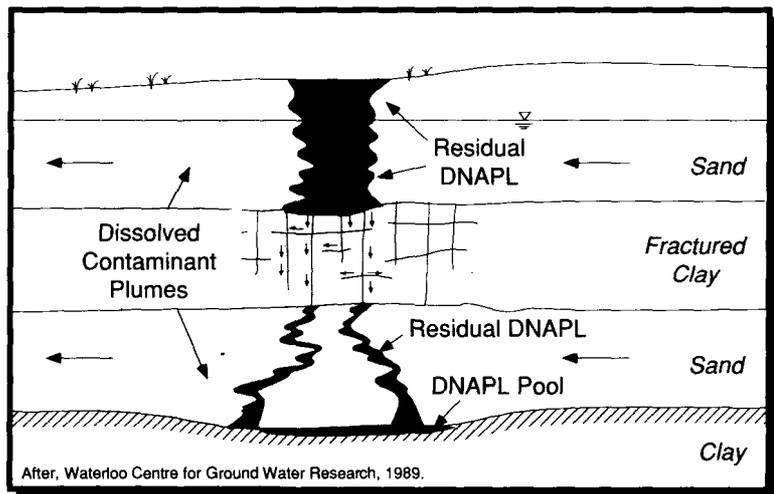
Case 5: Fractured Rock or Fractured Clay System

DNAPL introduced into a fractured rock or fractured clay system follows a complex pathway based on the distribution of fractures in the original matrix. The number, density, size, and direction of the fractures usually cannot be determined due to the extreme heterogeneity of a fractured system and the lack of economical aquifer characterization technologies. Relatively small volumes of DNAPL can penetrate deeply into fractured systems due to the low retention capacity of the fractures and the ability of some DNAPLs to migrate through very small (< 20 microns) fractures. Many clay units, once considered to be relatively impermeable to DNAPL migration, often act as fractured media with preferential pathways for vertical and horizontal DNAPL migration.

After, Waterloo Centre for Ground Water Research, 1989.
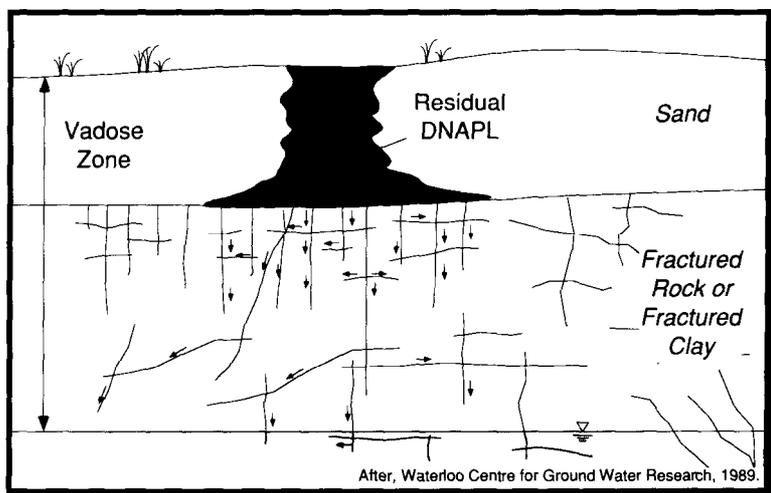
Does Historical Site Use Information Indicate Presence of DNAPL?
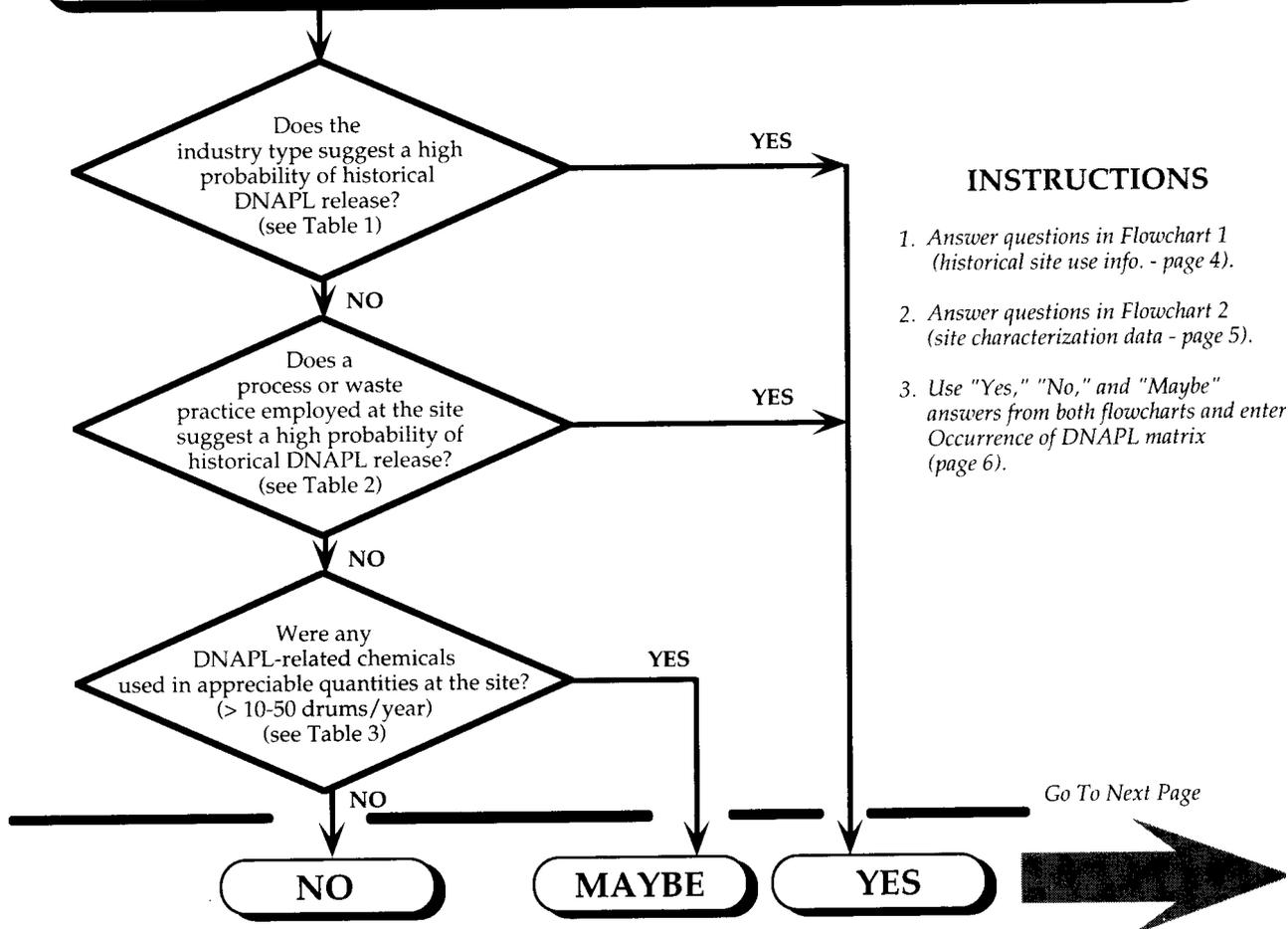
Occurrence of DNAPL - Decision Chart 1

Does the industry type suggest a high probability of historical DNAPL release? (see Table 1) — **YES**

NO ↓

Does a process or waste practice employed at the site suggest a high probability of historical DNAPL release? (see Table 2) — **YES**

NO ↓

Were any DNAPL-related chemicals used in appreciable quantities at the site? (> 10-50 drums/year) (see Table 3) — **YES**

NO ↓

NO   **MAYBE**   **YES**

Go To Next Page

INSTRUCTIONS

1. Answer questions in Flowchart 1 (historical site use info. - page 4).

2. Answer questions in Flowchart 2 (site characterization data - page 5).

3. Use "Yes," "No," and "Maybe" answers from both flowcharts and enter Occurrence of DNAPL matrix (page 6).

TABLE 1

Industries with high probability of historical DNAPL release:

- Wood preservation (creosote)
- Old coal gas plants (mid-1800s to mid-1900s)
- Electronics manufacturing
- Solvent production
- Pesticide manufacturing
- Herbicide manufacturing
- Airplane maintenance
- Commercial dry cleaning
- Instrument manufacturing
- Transformer oil production
- Transformer reprocessing
- Steel industry coking operations (coal tar)
- Pipeline compressor stations

TABLE 2

Industrial processes or waste disposal practices with high probability of historical DNAPL release:

- Metal cleaning/decreasing
- Metal machining
- Tool-and-die operations
- Paint removing/stripping
- Storage of solvents in underground storage tanks
- Storage of drummed solvents in uncontained storage areas
- Solvent loading and unloading
- Disposal of mixed chemical wastes in landfills
- Treatment of mixed chemical wastes in lagoons or ponds

TABLE 3 DNAPL-Related Chemicals (20):

Halogenated Volatiles

Chlorobenzene
1,2-Dichloropropane
1,1-Dichloroethane
1,1-Dichloroethylene
1,2-Dichloroethane
Trans-1,2-Dichloroethylene
Cis-1,2-Dichloroethylene
1,1,1-Trichloroethane
Methylene Chloride
1,1,2-Trichloroethane
Trichloroethylene
Chloroform
Carbon Tetrachloride
1,1,2,2-Tetrachloroethane
Tetrachloroethylene
Ethylene Dibromide

Halogenated Semi-Volatiles

1,4-Dichlorobenzene
1,2-Dichlorobenzene
Aroclor 1242, 1254, 1260
Chlordane
Dieldrin
2,3,4,6-Tetrachlorophenol
Pentachlorophenol

Non-Halogenated Semi-Volatiles

2-Methyl Napthalene
o-Cresol
p-Cresol
2,4-Dimethylphenol
m-Cresol
Phenol
Naphthalene
Benzo(a)Anthracene
Fluorene
Acenaphthene
Anthracene
Dibenzo(a,h)Anthracene
Fluoranthene
Pyrene
Chrysene
2,4-Dinitrophenol

Miscellaneous

Coal Tar
Creosote

Note: Many of these chemicals are found mixed with other chemicals or carrier oils.
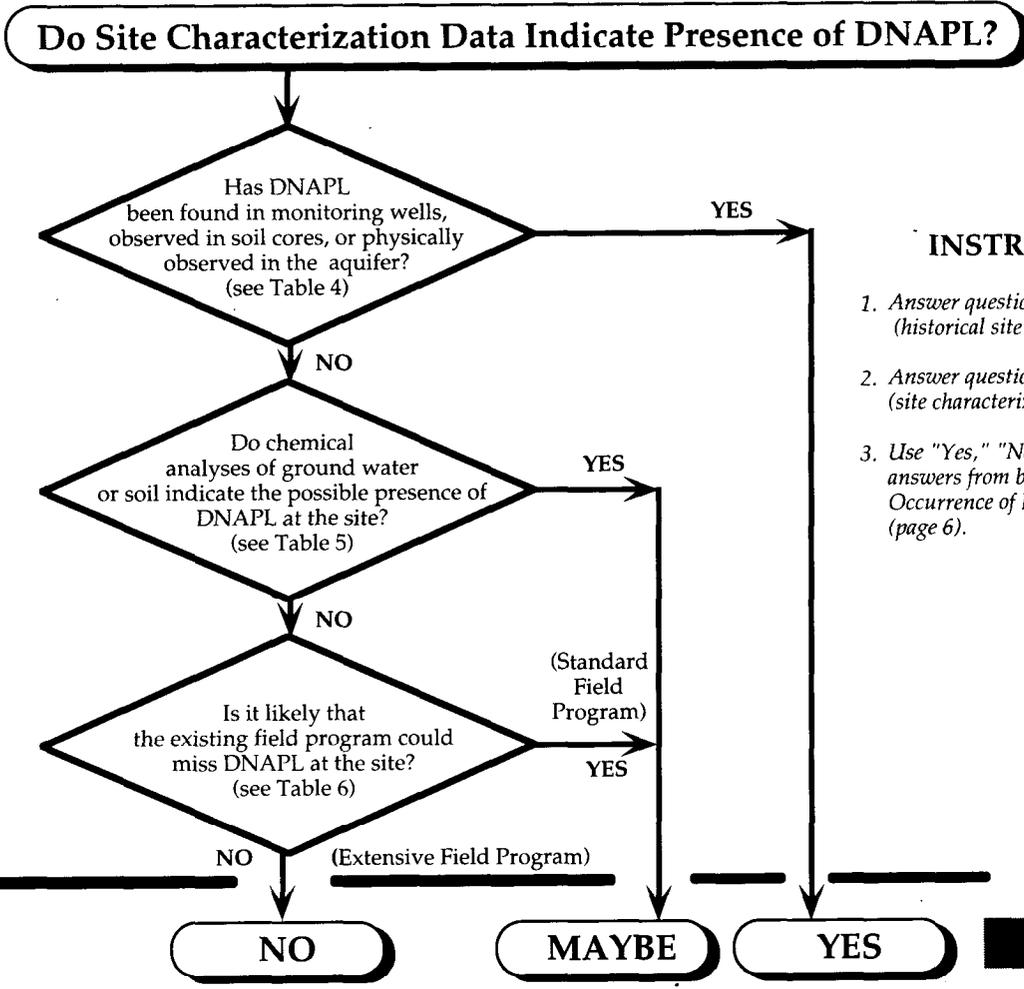
Note:
The potential for DNAPL release increases with the size and active period of operation for a facility, industrial process, or waste disposal practice.

Occurrence of DNAPL – Decision Chart 2

Do Site Characterization Data Indicate Presence of DNAPL?

Has DNAPL been found in monitoring wells, observed in soil cores, or physically observed in the aquifer? (see Table 4) → YES

NO ↓

Do chemical analyses of ground water or soil indicate the possible presence of DNAPL at the site? (see Table 5) → YES

NO ↓

(Standard Field Program)

Is it likely that the existing field program could miss DNAPL at the site? (see Table 6) → YES

NO → (Extensive Field Program)

NO   **MAYBE**   **YES**

Go To Next Page →

INSTRUCTIONS

1. *Answer questions in Flowchart 1 (historical site use info. - page 4).*

2. *Answer questions in Flowchart 2 (site characterization data - page 5).*

3. *Use "Yes," "No," and "Maybe" answers from both flowcharts and enter Occurrence of DNAPL matrix (page 6).*

TABLE 4

Methods to confirm DNAPL in wells:

- NAPL/water interface probes that signal a change in conductivity of the borehole fluid
- Weighted cotton string lowered down well
- Pumping and inspecting recovered fluid
- Transparent bottom-loading bailers
- Mechanical discrete-depth samplers.

In general, the depth of DNAPL accumulation does not provide quantitative information regarding the amount of DNAPL present (24).

Methods to confirm DNAPL in soil samples

Visual examination of cores or cuttings may not be effective for confirming the presence of DNAPL except in cases of gross DNAPL contamination. Methods for enhancing visual inspection of soil samples for DNAPL include:

- Shaking soil samples in a jar with water to separate the DNAPL from the soil (14).
- Performing a paint filter test, in which soil is placed in a filter funnel, water is added, and the filter is examined for separate phases (20).

TABLE 5

Conditions that indicate potential for DNAPL at site based on laboratory data:

Condition 1:
Concentrations of DNAPL-related chemicals (see pg. 3) in ground water are> 1% of pure phase volubility or effective volubility, (defined in Worksheet 1, pg. 7) (25).

Condition 2:
Concentrations of DNAPL-related chemicals on soils are >10,000 mg/kg (equal to 1 % of soil mass) (6).

Condition 3:
Concentrations of DNAPL-related chemicals in ground water calculated from water/soil partitioning relationships and soil samples are > pure phase volubility or effective solubility(see Worksheet 2, pg. 7).

Condition 4
Concentrations of DNAPL-related chemicals in ground water **increase** with depth or appear in **anomalous** up gradient / across gradient locations (25).

TABLE 6

Characteristics of extensive field programs that can help indicate the presence or absence of DNAPL (if several are present, select "NO"):

- Numerous monitoring wells, with wells screened in topographic lows on the surface of fine-grained, relatively impermeable units.

- Multi-level sampling capability.

- Numerous organic chemical analyses of soil samples at different depths using GC or GC/MS methods.

- Well-defined site stratigraphy, using numerous soil borings, a cone penetrometer survey, or geophysics.

- Data from pilot tests or "early action" projects that indicate the site responds as predicted by conventional solute transport relationships, rather than responding as if additional sources of dissolved contaminants are present in the aquifer (11, 25).

Note: *This procedure is designed primarily for hydrogeologic settings comprised of gravel, sand, silt, or clay and may not be be applicable to karst or fractured rock settings.*

Potential for Occurrence of DNAPL at Superfund Sites

DNAPL Category

		Do Characterization Data Indicate Presence of DNAPL? (Chart 2)		
		Yes	Maybe	No
Does Historical Use Indicate Presence of DNAPL? (Chart 1)	Yes	I	I - II	II
	Maybe	I	II	II - III
	No	I	II	III

Category	Implications for Site Assessment
high potential for DNAPL at site.	• The risk of spreading contaminants increases with the proximity to a potential DNAPL zone. Special precautions should be taken to ensure that drilling does not create pathways for continued vertical migration of free-phase DNAPLs. In DNAPL zones, drilling should be suspended when a low-permeability unit or DNAPL is first encountered. Wells should be installed with short screens (< 10 feet). If required, deeper drilling through known DNAPL zones should be conducted only by using double or triple-cased wells to prevent downward migration of DNAPL. As some DNAPLs can penetrate fractures as narrow as 10 microns, special care must be taken during all grouting, cementing, and well sealing activities conducted in DNAPL zones. • In some hydrogeologic settings, such as fractured crystalline rock, it is impossible to drill through DNAPL with existing technology without causing vertical migration of the DNAPL down the borehole, even when double or triple casing is employed (2). • The subsurface DNAPL distribution is difficult to delineate accurately at some sites. DNAPL migrates preferentially through selected pathways (fractures, sand layers, etc.) and is affected by small-scale changes in the stratigraphy of an aquifer. Therefore, the ultimate path taken by DNAPL can be very difficult to characterize and predict. • In most cases, fine-grained aquitards (such as clay or silt units) should be assumed to permit downward migration of DNAPL through fractures unless proven otherwise in the field. At some sites it can be exceptionally difficult to prove otherwise even with intensive site investigations (2). • Drilling in areas known to be DNAPL-free should be performed before drilling in DNAPL zones in order to form a reliable conceptual model of site hydrogeology, stratigraphy, and potential DNAPL pathways. In areas where it is difficult to form a reliable conceptual model, an "outside-in" strategy may be appropriate: drilling in DNAPL zones is avoided or minimized in favor of delineating the outside dissolved-phase plume (2). Many fractured rock settings may require this approach to avoid opening further pathways for DNAPL migration during site-assessment.
[I Moderate potential for DNAPL at site.	l Due to the potential risk for exacerbating ground-water contamination problems during drilling through DNAPL zones, the precautions described for Category I should be considered during site assessment. Further work should focus on determining if the site is a "DNAPL site."
III Low potential for DNAPL at site.	l DNAPL is not likely to be a problem during site characterization, and special DNAPL precautions are probably not needed. Floating free-phase organics (LNAPLs), sorption, and other factors can complicate site assessment and remediation activities, however.

Worksheet 1: Calculation of Effective Volubility (from Shiu, 1988; Feenstra, Mackay, & Cherry, 1991)

For a single-component DNAPL, the pure-phase volubility of the organic constituent can be used to estimate the theoretical upper-level concentration of organics in aquifers or for performing dissolution calculations. For DNAPLs comprised of a mixture of chemicals, however, the **effective volubility** concept should be employed:

$$S_i^e = X_i \, S_i$$

Where

S_i^e = the effective volubility (the theoretical upper-level dissolved-phase concentration of a constituent in ground water in equilibrium with a mixed DNAPL; in mg/1)

X_i = the mole fraction of component i in the DNAPL mixture (obtained from a lab analysis of a DNAPL sample or estimated from waste characterization data)

S_i = the pure-phase volubility of compound i in mg/1 (usually obtained from literature sources)

For example, if a laboratory analysis indicates that the mole fraction of trichloroethylene (TCE) in DNAPL is 0.10, then the effective solubility would be 110 mg/1 [pure phase solubility of TCE times mole fraction TCE: (1100 mg/1) * (0.10) = 110 mg/1]. Effective solubilities can be calculated for all components in a DNAPL mixture. Insoluble organics in the mixture (such as long-chained alkanes) will reduce the mole fraction and effective volubility of more soluble organics but will not contribute dissolved-phase organics to ground water. *Please* note *that this relationship is approximate and does not account for non-ideal behavior* of *mixtures, such as co-solvency, etc.*

Worksheet 2: Method for Assessing Residual NAPL Based on Organic Chemical Concentrations in Soil Samples (From Feenstra, Mackay, and Cherry, 1991)

To estimate if NAPLs are present, a partitioning calculation based on chemical and physical analyses of soil samples from **the saturated zone** (from cores, excavations, etc.) can be applied. This method tests the assumption that all of the organics in the subsurface are either dissolved in ground water or adsorbed to soil (assuming dissolved-phase sorption, not the presence of NAPL). By using the concentration of organics on the soil and the partitioning calculation, a theoretical pore-water concentration of organics in ground water is determined. If the theoretical pore-water concentration is greater than the estimated volubility of the organic constituent of interest, then NAPL may be present at the site. A worksheet for performing this calculation is presented below; see Feenstra, Mackay, and Cherry (1991) for the complete methodology.

Step 1: Calculate S_i^e, the effective volubility of organic constituent of interest.   See Worksheet 1, above.

Step 2: Determine **Koc,** the organic carbon-water partition coefficient from one of the following:
   A) Literature sources (such as 22) or
   B) From empirical relationships based on **Kow,** the octanol-water partition coefficient, which is also found in the literature (22). For example, **Koc** can be estimated from Kow using the following expression developed for polyaromatic hydrocarbons (8):

$$\text{Log Koc} = 1.0 * \text{Log Kow} - 0.21$$

Other empirical relationships between Koc and Kow are presented in refs. 4 and 15.

Step 3: Determine **foc,** the fraction of organic carbon on the soil, from a laboratory analysis of clean soils from the site. Values for **foc** typically range from 0.03 to 0.00017 mg/mg (4). Convert values reported in percent to mg/mg.

Step 4: Determine or estimate ρb, the dry bulk density of the soil, from a soils analysis. Typical values range from 1.8 to 2.1 g/ml (kg/l). Determine or estimate φw, the water-filled porosity.

Step 5: Determine **Kd,** the partition (or distribution) coefficient between the pore water (ground water) and the soil solids:

$$\text{Kd} = \text{Koc} * \text{foc}$$

Step 6 Using **Ct,** the measured cone. of the organic compound in saturated soil in mg/kg, calculate the theoretical pore water cone. assuming no DNAPL (i.e., Cw in mg/1):

$$Cw = \frac{(Ct * \rho b)}{(Kd * \rho b + \varphi w)}$$

Step 7 Compare **Cw** and S_i^e (from Step 1):

$Cw > S_i^e$ suggests possible **presence** of DNAPL

$Cw < S_i^e$ suggests possible **absence** of DNAPL

GLOSSARY (adapted from Cherry, 1991):

DNAPL: A Dense Nonaqueous Phase Liquid. A DNAPL can be either a single-component DNAPL (comprised of only one chemical) or a mixed DNAPL (comprised of several chemicals). DNAPL exists in the subsurface as free-phase DNAPL or as residual DNAPL (see following definitions). DNAPL does not refer to chemicals that are dissolved in groundwater.

DNAPL ENTRY LOCATION: The area where DNAPL has entered the subsurface, such as a spill location or waste pond.

DNAPL SITE: A site where DNAPL has been released and is now present in the subsurface as an immiscible phase.

DNAPL ZONE: The portion of a site affected by free-phase or residual DNAPL in the subsurface (either the unsaturated zone or saturated zone). The DNAPL zone has organics in the vapor phase (unsaturated zone), dissolved phase (both unsaturated and saturated zone), and DNAPL phase (both unsaturated and saturated zone).

DISSOLUTION: The process by which soluble organic components from DNAPL dissolve in ground water or dissolve in infiltration water and form a ground-water contaminant plume. The duration of remediation measures (either clean-up or long-term containment) is determined by 1) the rate of dissolution that can be achieved in the field, and 2) the mass of soluble components in the residual DNAPL trapped in the aquifer.

EFFECTIVE SOLUBILITY: The theoretical aqueous volubility of an organic constituent in ground water that is in chemical equilibrium with a mixed DNAPL (a DNAPL containing several organic chemicals). The effective volubility of a particular organic chemical can be estimated by multiplying its mole fraction in the DNAPL mixture by its pure phase volubility (see Worksheet 1, page 7).

FREE-PHASE DNAPL: Immiscible liquid existing in the subsurface with a positive pressure such that it can flow into a well. If not trapped in a pool, free-phase DNAPL will flow vertically through an aquifer or laterally down sloping fine-grained stratigraphic units. Also called mobile DNAPL or continuous-phase DNAPL.

PLUME: The zone of contamination containing organics in the dissolved phase. The plume usually will originate from the DNAPL zone and extend downgradient for some distance depending on site hydrogeologic and chemical conditions. To avoid confusion, the term "DNAPL plume" should not be used to describe a DNAPL pool; "plume" should be used only to refer to dissolved-phase organics.

POOL and LENS: A pool is a zone of free-phase DNAPL at the bottom of an aquifer. A lens is a pool that rests on a fine-grained stratigraphic unit of limited areal extent. DNAPL can be recovered from a pool or lens if a well is placed in the right location.

RESIDUAL DNAPL: DNAPL held in soil pore spaces or fractures by capillary forces (negative pressure on DNAPL). Residual will remain trapped within the pores of the porous media unless the viscous forces (caused by the dynamic force of water against the DNAPL) are greater than the capillary forces holding the DNAPL in the pore. At most sites the hydraulic gradient required to mobilize all of the residual trapped in an aquifer is usually many times greater than the gradient that can be produced by wells or trenches (26).

RESIDUAL SATURATION: The saturation (the fraction of total pore space containing DNAPL) at which DNAPL becomes discontinuous and is immobilized by capillary forces (14). In unsaturated soils, residual saturation typically ranges from 5% to 20% of total pore volume, while in the saturated zone the residual saturation is higher, with typical values ranging from 15% to 50% of total pore volume (14,17). At many sites, however, DNAPL migrates preferentially through small-scale fractures and heterogeneities in the soil, permitting the DNAPL to penetrate much deeper than would be predicted from application of typical residual saturation values (16).

Defined Areas at a DNAPL Site

DNAPL ZONE (contains free-phase DNAPL in pools or lenses and/or residual DNAPL)

Dissolved-Phase PLUME

DNAPL ENTRY LOCATION (such as a former waste pond)

Ground Water Flow Direction
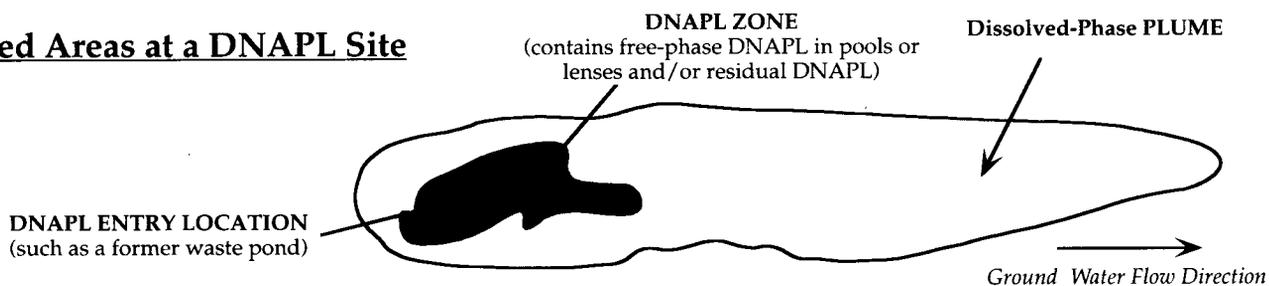
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EXAMPLES

EXAMPLE 1: TIER 1: LEAKING PETROLEUM STORAGE SITE (LPST) 96497 MW-5

Input Data:

Data Type	Parameter	Value	Source of Data
Concentration	• Benzene Concentration	Date Conc (mg/L) 9/19/1995 2.7 12/27/1995 2.2 4/14/1996 3.2 7/15/1997 2.4 10/9/1997 2 1/19/1998 1.8 4/20/1998 1.31 7/20/1998 2.081 10/4/1998 2.187 4/6/1999 1.4 10/18/1999 0.48 1/26/2000 0.95 4/6/2000 0.62 10/26/2000 0.64	• Groundwater sampling
Cleanup Level	• MCL	Benzene: 0.005 (mg/L)	• Regulatory Agency
OUTPUT	• Predicted time to achieve cleanup • 95 percent confidence interval • Source decay rate constant	• 2016 • 2009-2031 • 0.317 1/yr	See Figure 1-1

SourceDK Modeling Summary, LPST:

- SourceDK was used to estimate the groundwater remediation timeframe and uncertainties associated with the estimated timeframe for benzene at a leaking petroleum storage tank site.

- Tier 1 was used as the primary model to predict the remediation timeframe by plotting log concentration of the historical monitoring data vs. time and then extrapolating to estimate how long it will take to achieve a cleanup goal, assuming the current trend continues.

- Historical well monitoring data from 1995 to 2000 were entered in Section 1 and the remediation timeframe to achieve a MCL of 0.005 mg/L for benzene was determined.

KEY POINT:

A logarithmic extrapolation of the concentration versus time trend results in a predicted time to achieve cleanup in the year 2016. The estimated range in this prediction, based on the consistency of the trend, is from the year 2009 to 2031.

Figure 1-1. SourceDK Input/Output Screen. Leaking Petroleum Storage Tank Site.

EXAMPLE 2: TIER 2: PETROLEUM REFINERY

Input Data:

Data Type	Parameter	Value	Source of Data
Advection	• Darcy velocity	50-200(ft/yr)	• Initial range, final value from calibration of concentration vs. time data
Source Data	• Source Length: • Source Width: • Source Thickness: • Average Source Groundwater Concentration: • Specific Discharge:	100 (ft) 100 (ft) 5 (ft) 16 (mg/L) Calculated using SourceDK	• Based on geologic logs and lumped BTEX monitoring data • Based on BTEX groundwater monitoring data
Source Mass	• Source mass:	220(kg)	• Estimated from field data.
Concentration	• Benzene Concentration	Time (yr) Conc (mg/L) 0 16.0 2 6.0 3 7.4 5 1.26 6 0.77 8 1.0 9 1.4 11 0.91 12 1.3 13 0.876 14 0.548 15 0.74	• Groundwater sampling
Biodegradation	Electron Acceptor: Upgradient Conc. (mg/L): Source Conc. (mg/L): Change in Conc. (mg/L): Electron Acceptor: Avg. Conc. (mg/L): Percent of Biodegradation Capacity Applied to This Constituent	O_2 NO3 SO4 1.40 1.0 1060 - 0.22 - 0.05 - 392 **1.18** **0.95** **668** Fe CH4 **0.01** **0.12** 25% Note: Bold values are SourceDK input values.	• Groundwater sampling • Based on sampling (equal proportions of benzene, toluene, ethylbenzene, and xylenes present.)
OUTPUT	Attenuation timeframe:	33 yrs to reach 0.005 mg/L A factor of 2 uncertainty in the mass estimation gives a range of 16 - 66 yrs to reach the target concentration.	See Figure 2-2

EXAMPLE 2

SourceDK Modeling Summary, Petroleum Refinery:

- SourceDK was used to estimate the groundwater remediation timeframe and uncertainties associated with the estimated timeframe for benzene at a petroleum refinery.

- Tier 2 was used as the primary model to predict the remediation timeframe because of the availability of site hydrogeological data.

- Site hydrogeological data was entered in Section 1 and source characteristics in Section 2. Specific discharge and source decay constant were calculated using SourceDK.

- Source Mass Method 1 was used to calculate the source zone mass to be used in the calculation of the source decay constant.

- Site specific source zone biodegradation data were entered in Section 3B.

- An uncertainty of ± a factor of 2 was assumed in the mass calculations.

- Investigations documented the occurrence of BTEX in wells located within several hundred feet downgradient of the inferred source within a ten year period, suggesting a velocity of at least 50 ft/yr. However, studies also noted the bedrock at the site to be extensively fractured, which could result in significantly faster contaminant transport. For this purpose, a Darcy velocity ranging from 50 to 200 ft/yr was assumed. A Darcy velocity of 75 ft/yr predicted a model that fit the historical concentration data fairly well.

- The Tier 2 input screen is shown in Figure 2-1.

KEY POINT:

A deterministic model indicates that 33 years (a factor of 2 uncertainty in the mass gives a range of 16 – 66 years) will be required at this flowrate to remove mass from the source zone and for biodegradation to remove dissolved constituents from the source zone so that the desired cleanup level can be reached.

EXAMPLE 2

Figure 2-1. SourceDK Tier 2 Input Screen. Petroleum Refinery.

Figure 2-2. SourceDK Tier 2 Output. Petroleum Refinery.

EXAMPLE 3: TIER 2: ABC CHEMICAL MANUFACTURING COMPANY

Input Data:

Data Type	Parameter	Value	Source of Data
Hydrogeology	• Hydraulic Conductivity: • Hydraulic Gradient: • Porosity:	5.17×10^{-2} (cm/sec) 0.00139 (ft/ft) 0.25 (-)	• Slug-tests results • Static water level measurements • Estimated
Advection	• Darcy velocity: • Retardation:	74 (ft/yr) 1.2 (-)	• Calculated • Calculated
Adsorption	• Saturated Soil Density:	1.9 (kg/L)	• Estimated
Source Data	• Source Length: • Source Width: • Source Thickness: • Source Mass: • Specific Discharge:	700 (ft) 480 (ft) 50 (ft) Calculated using SourceDK Calculated using SourceDK	• Based on area of affected groundwater plume
Concentration	• TCE Concentration	Time (yr) Conc (mg/L) 0 0.33 0.4 0.33 1.1 0.28 1.4 0.34 1.7 0.24 2.7 0.20 3.6 0.17 5.2 0.18	• Groundwater sampling
Biodegradation	• Biodegradation Rate Constant	4.4 (1/yr)	• Initial value from literature; final value from calibration of concentration vs time data.
OUTPUT	Attenuation timeframe	27 yrs to reach 0.005 mg/L A factor of 10 uncertainty in the mass estimation gives a range of 3 - 270 yrs to reach the target concentration.	See Figure 3-6

SourceDK Modeling Summary:

- SourceDK was used to estimate the groundwater remediation timeframe and the uncertainties associated with the estimated timeframe for the trichloroethene (TCE) plume at a Chemical Manufacturing facility.

- Tier 2 was used as the primary model to predict the remediation timeframe by estimating the source attenuation from a source mass estimate, the mass flux of constituents leaving the source zone, and the biodegradation processes in the source zone.

- Site hydrogeological data was entered in Section 1 and source characteristics in Section 2.

EXAMPLE 3

- Specific discharge, source decay constant, and source mass were calculated using SourceDK.

- Source Mass Method 3 was used to calculate the source zone mass. The area-weighted average method was employed to calculate the source mass. For this purpose, concentrations and the areas associated with these concentrations were entered separately for the saturated NAPL and dissolved phases (Figure 3-2 through Figure 3-5).

- The biodegradation rate constant data entered in Method 1 of Section 3B.

- Initially, a dissolved phase biodegradation rate constant, λ, of 4.4 per year was used. However, the initial run indicated that the source zone concentration was decaying too rapidly compared to the observed monitoring data. Therefore, λ was adjusted until SourceDK matched the observed decay. The final dissolved phase biodegradation rate constant was 1.2 per year.

- An uncertainty of ± a factor of 10 was assumed in the mass calculations.

KEY POINT:

A deterministic model indicates that 27 years (the factor of 2 uncertainty in the mass give a range of 13 – 54 years) will be required at this flowrate to remove mass from the source zone and for biodegradation to remove dissolved constituents from the source zone so that the desired cleanup level of 0.005 mg/L can be reached.

EXAMPLE 3

Figure 3-1. SourceDK Tier 2 Chlorinated Solvent Site Input. ABC Manufacturing.

Figure 3-2. SourceDK Tier 2 Source Mass Calculation Input. The user selects an option for averaging concentration data. ABC Manufacturing.

SourceDK Tier 2 Mass Method 3: Layer Shape and Dimension Calculation

Site: ABC Chem Manufacturing

Constituent: TCE

Layer Name: Saturated Zone NAPL

Calculation Method: Area-Weighted Average

1. Enter Layer Dimensions

Layer Thickness   20   *(ft)*

2. Enter Concentration and Areas for Each Sample in this Layer

	Concentration (mg/kg)	Area (ft^2)		Concentration (mg/kg)	Area (ft^2)		Concentration (mg/kg)	Area (ft^2)
1	30.000	1125	11			21		
2	65.000	1130	12			22		
3	25.000	1198	13			23		
4	17.000	1160	14			24		
5	18.600	1216	15			25		
6	38.000	1246	16			26		
7	42.000	1160	17			27		
8	48.000	1128	18			28		
9			19			29		
10			20			30		

Return

Clear Screen

HELP

Source Mass: 354.77   *(kg)*

Figure 3-3. SourceDK Tier 2 Saturated NAPL Layer Mass Calculation Input. In this method the user enters the concentration and the representative area for that concentration. ABC Manufacturing.

SourceDK Tier 2 Mass Method 3: Layer Shape and Dimension Calculation

Site: ABC Chem Manufacturing
Constituent: TCE

Layer Name: Dissolved Constituents
Calculation Method: Area-Weighted Average

1. Enter Layer Dimensions

Layer Thickness   40   (ft)

2. Enter Concentration and Areas for Each Sample in this Layer

	Concentration (mg/L)	Area (ft^2)		Concentration (mg/L)	Area (ft^2)		Concentration (mg/L)	Area (ft^2)
1	18.000	1159	11			21		
2	21.500	1188	12			22		
3	23.500	1156	13			23		
4	22.000	1148	14			24		
5	17.600	1198	15			25		
6	12.600	1176	16			26		
7	9.700	1169	17			27		
8	13.500	1156	18			28		
9			19			29		
10			20			30		

Return

Source Mass: 45.78   (kg)

Clear Screen

HELP

Figure 3-4. SourceDK Tier 2 Dissolved Phase Layer Mass Calculation Using the Area-Weighted Average Method. In this method the user enters the concentration and the representative area for that concentration. ABC Manufacturing.

SourceDK Tier 2 Mass Method 3
Detailed Volume X Concentration Calculation

Site: ABC Chem Maufacturing
Constituent: TCE

Data Input Instructions:

| 115 | → *Enter value directly.* |

| Enter Data | → *Press button to enter layer data.* |

| 20 | → *Value calculated by model. (Don't enter any data).* |

1. Enter Site Data

Saturated Zone Porosity	0.25	(-)
Saturated Zone Soil Density	1.9	(g/cm^3)
Retardation Factor	1.2	(-)

2. Enter Zone Data

2a. Saturated Zone NAPL

Enter Data   ?

Set layer shape and dimensions

Mass of NAPL sorbed material in saturated zone   3.5E+02 (Kg)

2b. Dissolved Constituent

Enter Data   ?

Set layer shape and dimensions

Mass of dissolved constituent in saturated zone   4.6E+01 (Kg)

2c. Sorbed Constituent   9.2E+00 (Kg)

3. Calculation Results
Total mass of constituent   4.1E+02 (Kg)
(Sum of Saturated Zone NAPL, Dissolved Constituent, and Sorbed Constituent)

Calculate Sheet

Clear Screen

Paste Example Data Set

Return to Tier 2 Input

Help

Figure 3-5. SourceDK Tier 2 Dissolved Phase Layer Mass Calculation. ABC Manufacturing.

Figure 3-6. SourceDK Tier 2 Chlorinated Solvent Site Output. ABC Manufacturing.

EXAMPLE 4: TIER 3: PORE VOLUMES AND TIME REQUIRED TO FLUSH DISSOLVED ZONE

Input Data:

Data Type	Parameter	Value	Source of Data
Source Data	• Source Length Parallel to Groundwater Flow: • Original Constituent Concentration:	50 (ft) 50 (mg/L)	• Based on monitoring data
Desired Cleanup Level	• MCL	Benzene: 0.005 (mg/L)	
Groundwater Flow	• Seepage velocity:	100 (ft/yr)	• Calculated
Retardation Factor	• Soil Bulk Density: • Effective Porosity: • Fraction Organic Carbon: • Partition Coefficient: • Retardation Factor:	1.7 (kg/L) 0.35 (-) 0.00053 (-) 83 (L/kg) 1.21 (-)	• Estimated • Estimated • Lab analysis • Literature • Calculated using SourceDK
OUTPUT	Remediation Volume: Remediation Timeframe:	5.5 Pore Volumes 2.7 Years	See Figure 4-1

SourceDK Modeling Summary:

- SourceDK Tier 3 was used as the primary model to estimate the time and amount of naturally flowing groundwater required to remediate a source zone containing only dissolved constituents.

- Site specific data was entered in Method 1 of Tier 3.

- The retardation factor was calculated using SourceDK.

- Figure 4-1 shows the Tier 3 input and output data.

KEY POINT:

As shown in Figure 4-1, the time required for naturally occurring water to flush out the constituents in the dissolved phase is 2.7 yrs and the number of pore volumes required is 5.5. This estimate of time is conservative since the model does not account for biodegradation.

Figure 4-1. SourceDK Tier 3 Dissolved Phase Constituent. Chemical Manufacturing.

EXAMPLE 5:   TIER 3: PORE VOLUMES AND TIME REQUIRED TO FLUSH NAPL ZONE

Input Data:

Data Type	Parameter	Value	Source of Data
Source Data	• Source Length Parallel to Groundwater Flow: • Initial Aqueous Phase Concentration:	50 (ft) 50 (mg/L)	• Based on monitoring data • Based on monitoring data
Media Characteristics	• Type	Uniform fine sand	• Based on well logs
Desired Cleanup Level	• MCL	Benzene: 0.005 (mg/L)	
NAPL Characteristics	• Density of NAPL Fluid: • Initial NAPL Saturation in Porous Media:	1.5 (g/mL) 1 (%)	• Estimated • Estimated
Groundwater Flow	• Seepage velocity: • Seepage velocity while pumping:	100 (ft/yr) 200 (ft/yr)	• Calculated • Calculated
OUTPUT	Remediation Timeframe:	For Natural Attenuation: 197 years (with a range of 99 – 395 years for a factor of 2 uncertainty). For Pump-and- Treat: 140 years (with a range of 70 – 279 years for a factor of 2 uncertainty).	See Figure 5-1
OUTPUT	Remediation Pore Volumes:	For Natural Attenuation: 395 pore volumes (with a range of 197 – 789 for a factor of 2 uncertainty). For Pump-and- Treat: 558 pore volumes (with a range of 279 – 1,120 for a factor of 2 uncertainty).	See Figure 5-2

SourceDK Modeling Summary:

- SOURCEDK Tier 3 was used as the primary model to 1) estimate the time and amount of naturally flowing groundwater required to flush benzene from a NAPL source zone due to dissolution only (no biodegradation in source zone), and 2) to compare the relative impact of the cleanup time for natural attenuation vs. the pump-and-treat scenario.

- Site specific data was entered in Method 2 of Tier 3.

- An uncertainty of ± a factor of 2 was used in the estimation of the time and amount of naturally flowing groundwater required to flush the constituent from the source zone.

- Figure 4 shows the Tier 3 input and output data.

KEY POINT:

As shown in Figure 5-1, the time required for naturally occurring water to flush out the constituents, after accounting for the NAPL present, from the source zone is 197 years (with a range of 99 – 395 years for an uncertainty of a factor of 2 in the estimation of the NAPL saturation) (NAPL takes a long time to dissolve), whereas the number of pore volumes required is 395 (with a range of 197 – 789 for a factor of 2 uncertainty). This estimate of time is conservative since the model does not account for biodegradation.

For pumping systems, as shown in Figure 5-2, the time required to flush out the constituents, after accounting for the NAPL present, from the source zone is 140 years (with a range of 70 – 279 years for an uncertainty of a factor of 2), whereas the number of pore volumes required is 558 (with a range of 279 – 1120 for an uncertainty of a factor of 2). Pumping increases the flow, but it decreases the concentration. Therefore, even though the number of pore volumes almost doubles, the remediation time is not halved.

Note that the time and number of pore volumes required to remediate source zones containing NAPL is considerably larger than sources with dissolved phase constituents only because of the difficulty of flushing NAPL out.

Figure 5-1. SourceDK Tier 3 NAPL Zone Constituent Site Output: Natural Attenuation. Chemical Manufacturing.

Figure 5-2. SourceDK Tier 3 NAPL Zone Constituent Site Output: Pump and Treat. Chemical Manufacturing.

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