

540902500



Ground Water Issue

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

Charles J. Newell¹, Hanadi S. Rifai², John T. Wilson³, John A. Connor¹, Julia A. Aziz¹, and Monica P. Suarez²

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

¹Groundwater Services, Inc., Houston, Texas

²University of Houston, Texas

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



Recycled/Recyclable
Printed with vegetable-based ink on paper that contains a minimum of 50% post-consumer fiber content processed chlorine free.

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).

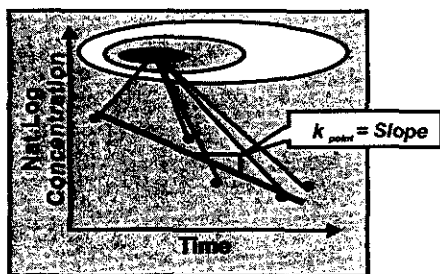


Figure 1. Determining concentration vs. time rate constant (k_{point}).

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).

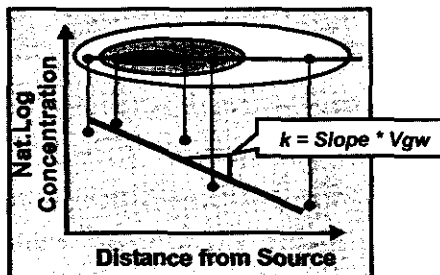


Figure 2. Determining concentration vs. distance rate constant (k).

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).

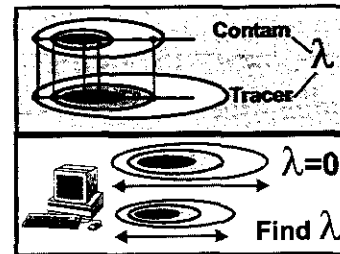


Figure 3. Determining biodegradation rate constant (λ).

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 = $0.693 / [\text{half-life}]$ and
 Half-life = $0.693 / [\text{rate constant}]$

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 Einerson 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

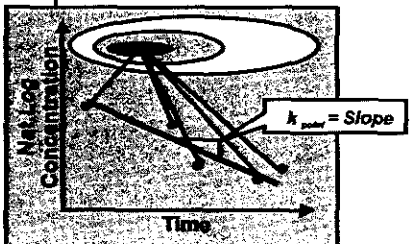
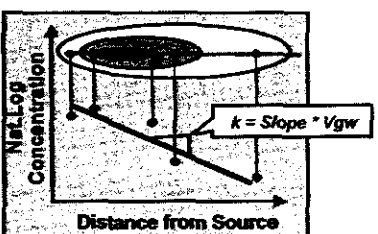
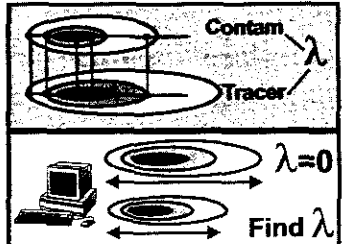
	Point Decay Rate Constant (k_{point})	Bulk Attenuation Rate Constant (k)	Biodegradation Rate Constant (λ)
USED FOR:	Plume Duration Estimate. Used to estimate time required to meet a remediation goal at a particular point within the plume. If wells in the source zone are used to derive k_{point} , then this rate can be used to estimate the time required to meet remediation goals for the entire site. k_{point} should not 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:	<p>Plot natural log of concentration vs. time for a single monitoring point and calculate $k_{point} = \text{slope of the best-fit line}$ (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.</p>  <p>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).</p>	<p>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:</p> <ol style="list-style-type: none"> 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. <p>Multiply this slope by the contaminant velocity (seepage velocity divided by the retardation factor R) to get k.</p> 	<p>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</p> <p>Calibrate a ground-water solute transport computer model that includes dispersion and retardation (e.g., BIOSCREEN, BIOCHLOR, BIOPLUME III, MT3D) by adjusting λ; or</p> <p>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.</p> 

Table 2. Continued...

	Point Decay Rate Constant (k_{point})	Bulk Attenuation Rate Constant (k)	Biodegradation Rate Constant (λ)
HOW TO USE:	<p>To estimate plume lifetime:</p> <p>The time (t) to reach the remediation goal at the point where K_{point} was calculated is:</p> $t = \frac{-\ln \left[\frac{C_{goal}}{C_{start}} \right]}{k_{point}}$	<p>To estimate if a plume is showing relatively little change:</p> <p>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:</p> $t = \frac{-\ln \left[\frac{C_{goal}}{C_{start}} \right]}{k}$ <p>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:</p> $L = \frac{V_s}{R} \cdot t$ <p>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.</p>	<p>To estimate if a plume is showing relatively little change:</p> <p>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.</p>
TYPICAL VALUES:	<p>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).</p> <p>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.</p>	<p>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 4) as the effects of dispersion and sorption will be small compared to biodegradation.</p>	<p>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 4 and 5).</p> <p>For more information about biodegradation rates for a variety of compounds, see Wiedemeier et al., 1999 and Suarez and Rifai, 1999.</p>

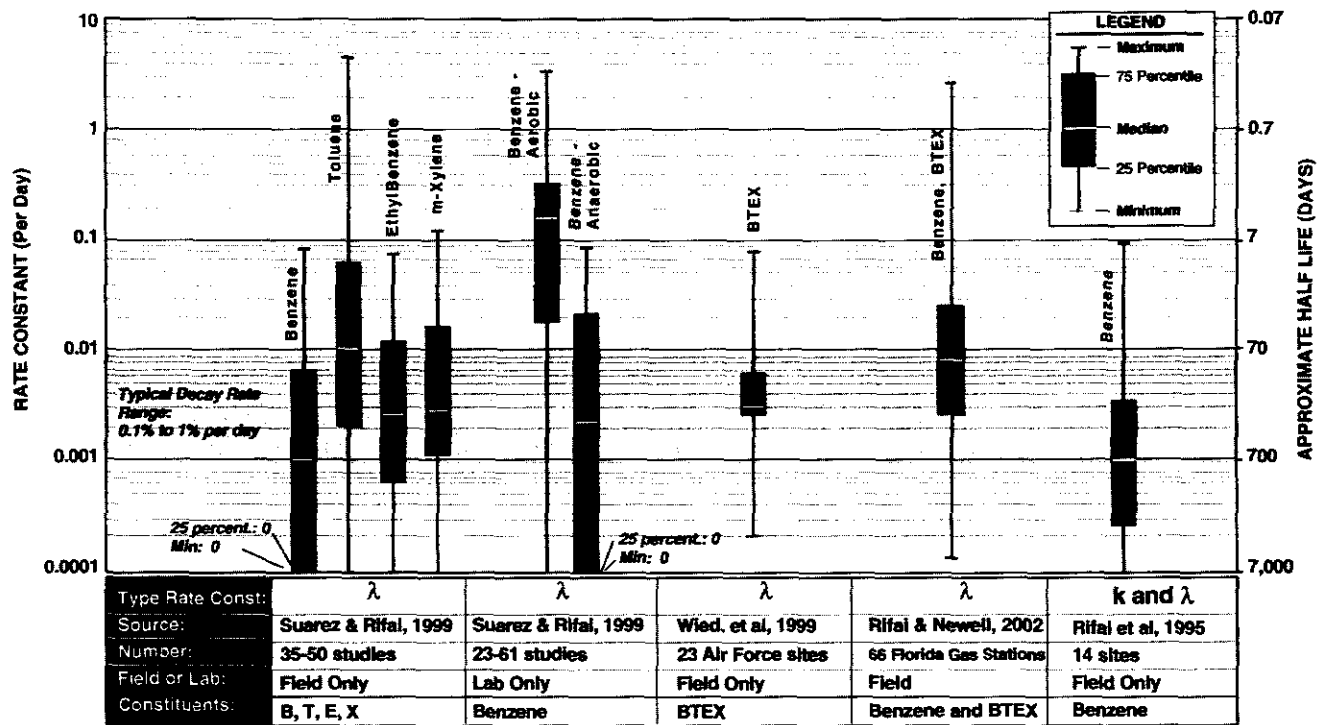


Figure 4. Biodegradation Rate Constants (λ) and Bulk Attenuation Rate Constants (k) for BTEX compounds from the literature. Source: Rifai and Newell, 2001.

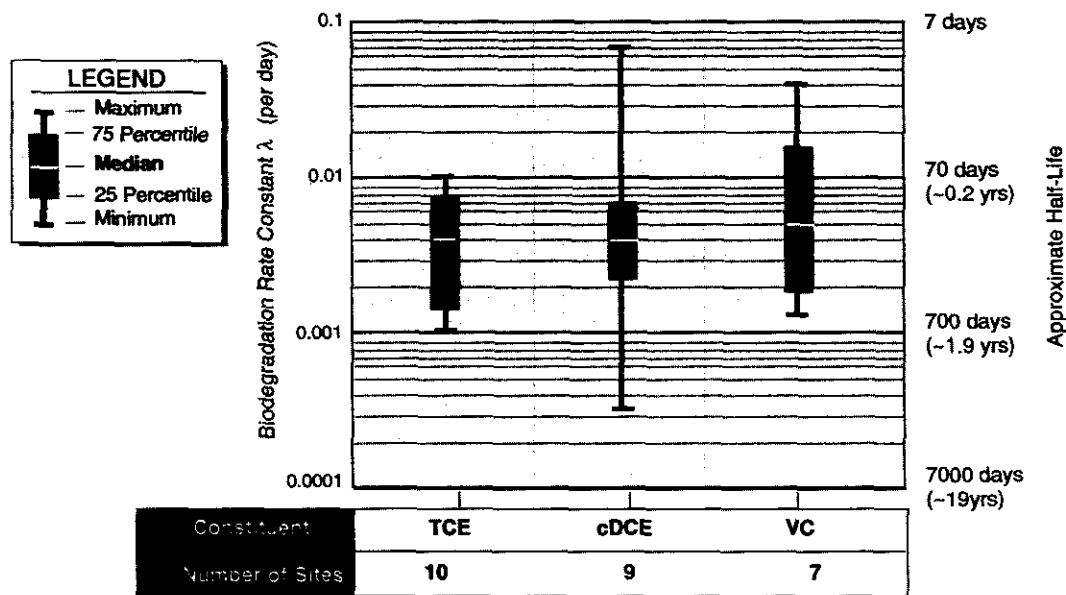


Figure 5. Biodegradation Rate Constants (λ) for Trichloroethene (TCE), cis-Dichloroethene (cDCE), and Vinyl Chloride (VC) compounds from BIOCHLOR modeling studies. Source: Aziz et al., 2000.

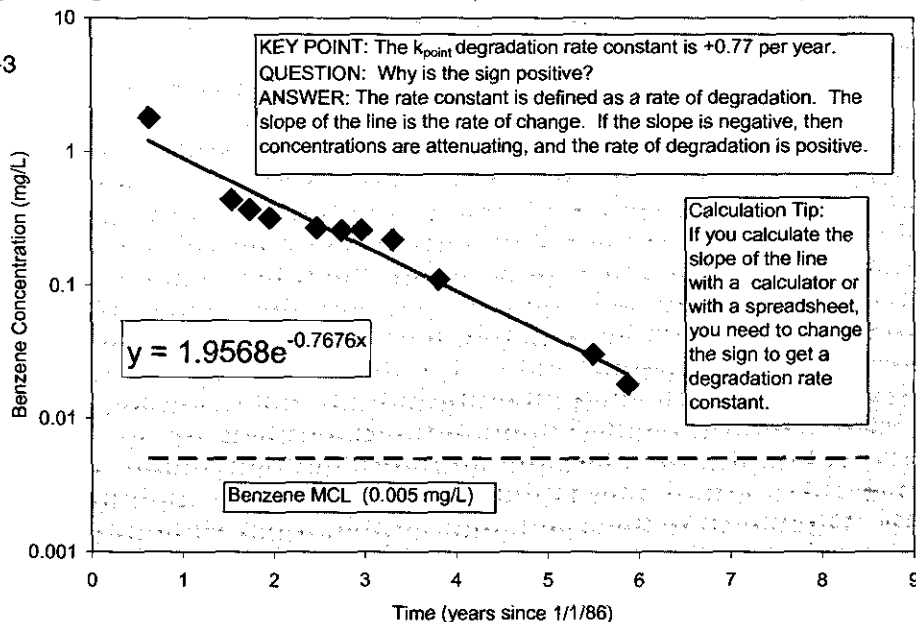
EXAMPLE 1. Use of Concentration vs. Time Rate Constants (k_{point})

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



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:

$$\ln(\text{Conc. Benzene}) = \exp^{(0.67 - 0.77x)} \text{ which resulted in the following rate equation:}$$

$$\text{Benzene concentration (mg/L)} = 1.96 \text{ mg/L} * \exp^{(-0.77 \text{ yrs since } 1/1/86)} \text{ where } k_{point} = +0.77 \text{ per year.}$$

Rearranging the equation:

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

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

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

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)

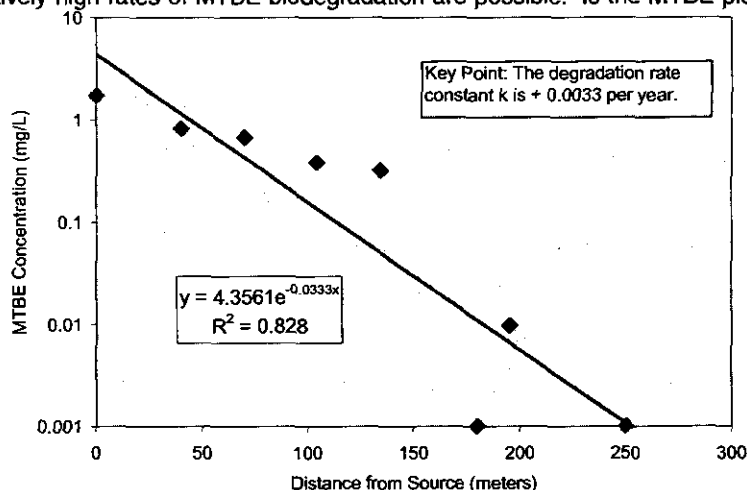
INTRODUCTION: This constant is estimated between wells along the inferred centerline of the plume. An MTBE plume at a former fuel farm located at a U.S. Coast Guard Base has a maximum source zone concentration of 1.740 mg/L of MTBE. The average calculated seepage velocity at the site was calculated to 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



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 yr). 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?

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.

Plume Trends?

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.

Plume Duration?

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).

INTRODUCTION: 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

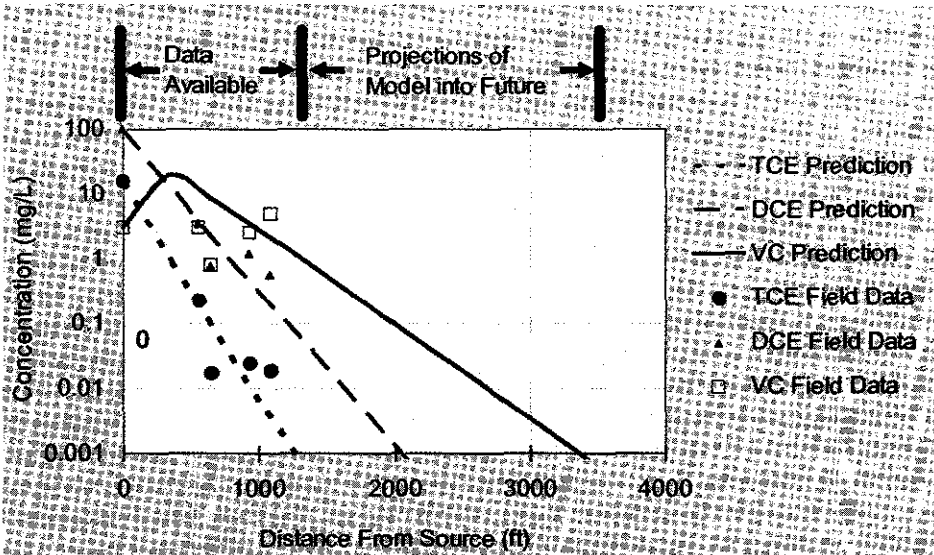
CALCULATION: The following approach was used to determine biodegradation rate constants for each of the chlorinated solvents using a solute transport model:

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 4 and 5), 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?

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.

Plume Trends?

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.

Plume Duration?

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 $1\mu\text{g/L}$, 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

Type of Uncertainty	Applies to	Type of Effect	Ways to Manage
Monitoring Well Location (horizontal and vertical location)	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.
Seasonal Effects	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.
Seepage Velocity Estimate	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).
Plume Heterogeneity	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 ($\mu\text{g/liter}$)	Concentration ($\mu\text{g/liter}$)	Concentration ($\mu\text{g/liter}$)
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

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

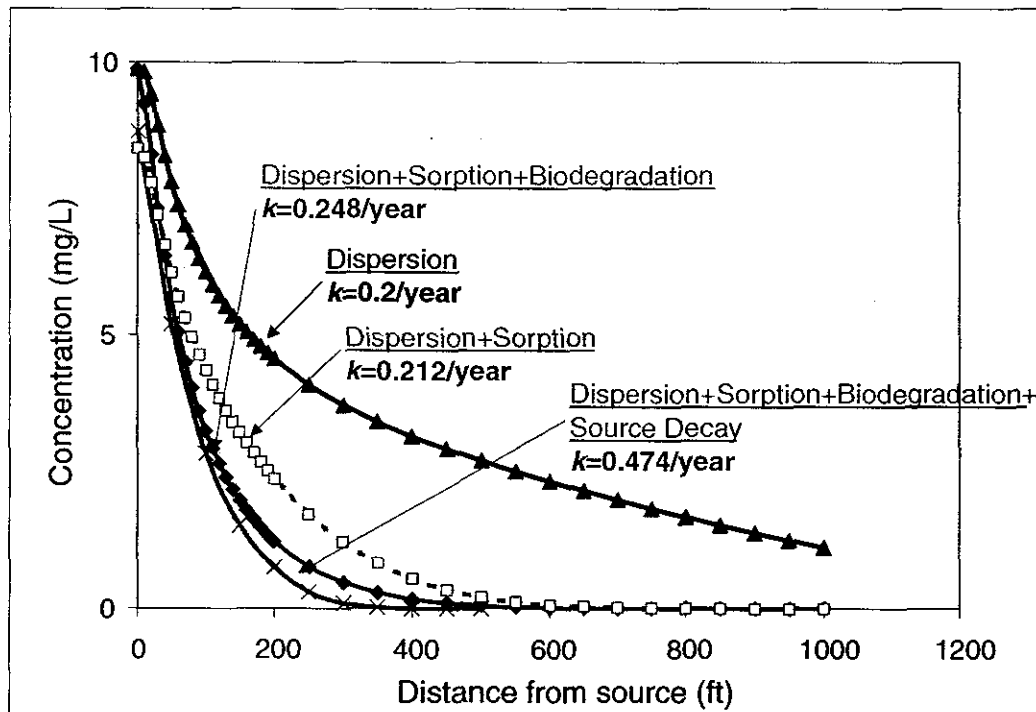
where C_0 is the initial concentration, α_x is the longitudinal dispersivity, α_y is the transverse dispersivity, λ is the biodegradation rate, t is time, x is distance from the source, v is the retarded ground-water velocity (i.e., $v = v_f/R$), and Y is source width.

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

$v = 100$ ft/yr (median value from the HGDB database (Newell et al., 1990))
 $Y = 40$ ft
 $t = 10$ years
 $\alpha_y = 0.1 \alpha_x$
 $b = 10$ 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 ($\alpha_x = 100$ ft); 2) previous scenario plus the effect of sorption ($R=5$); 3) dispersion, sorption, and biodegradation ($\lambda=0.2$ per yr) are acting; and 4) previous scenario plus the effect of source decay ($k_{\text{source}} = 0.139$ per yr).

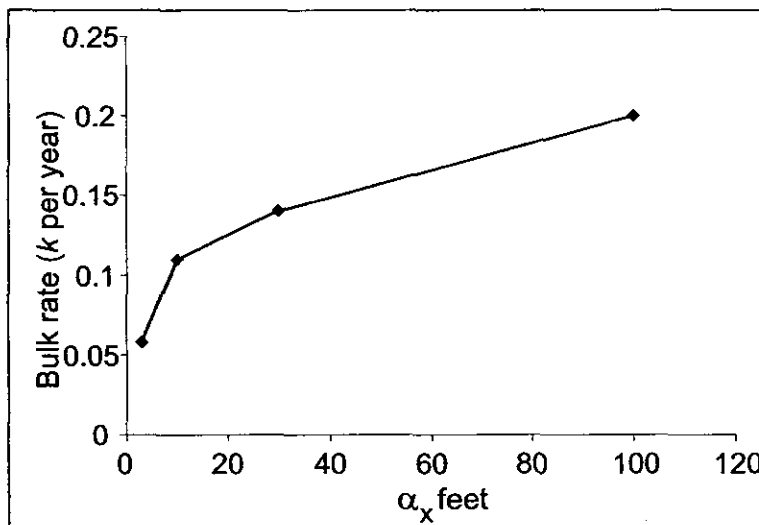
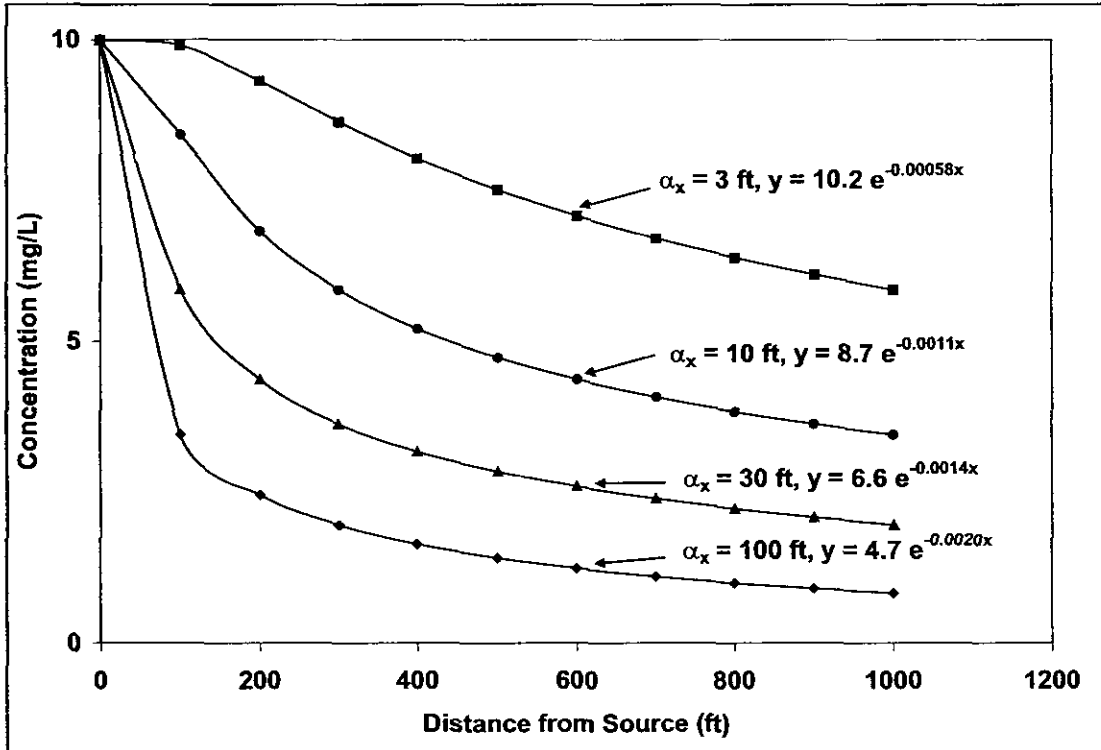
For each scenario, the Domenico solution was applied to obtain concentrations along the centerline of the plume. Next, concentrations vs. distance were plotted and data were fit with an exponential equation (first-order model). The slopes of the C vs. D plots were 0.002, 0.0106, 0.0124, and 0.0237/ft 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:

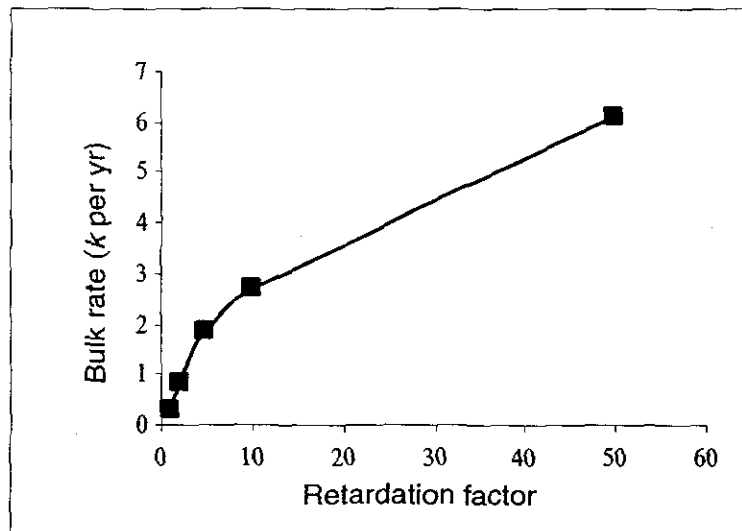
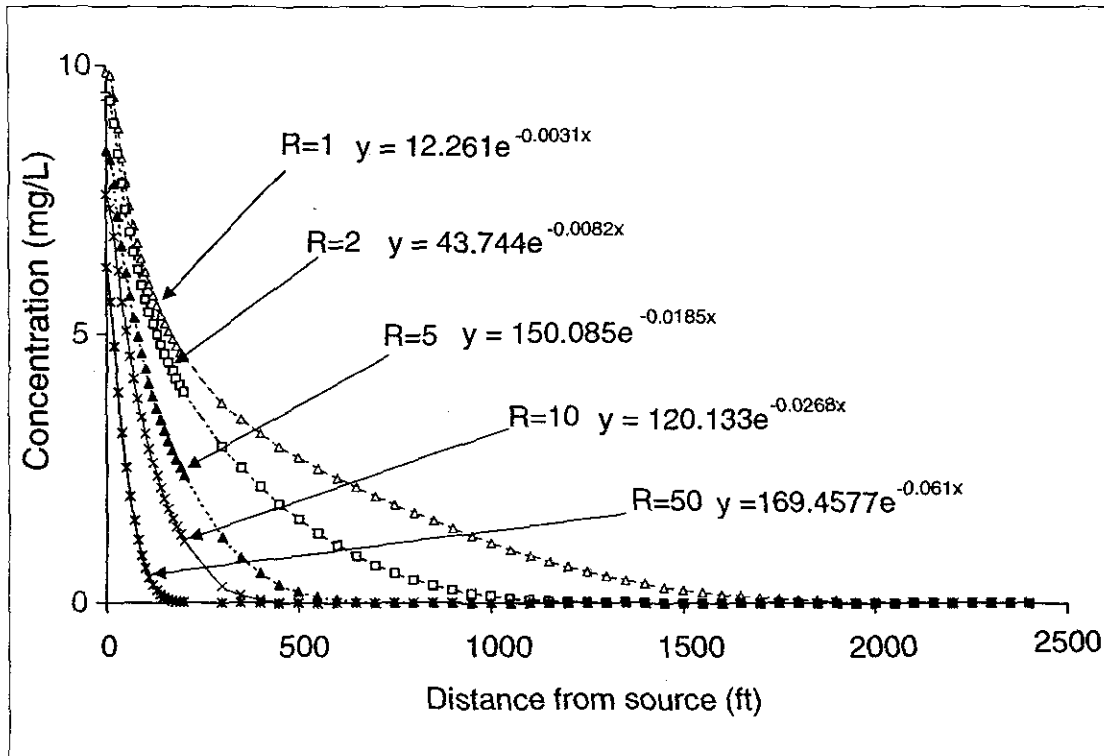
Bulk Attenuation Rate (k) as a Function of Longitudinal Dispersivity (α_x)

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.



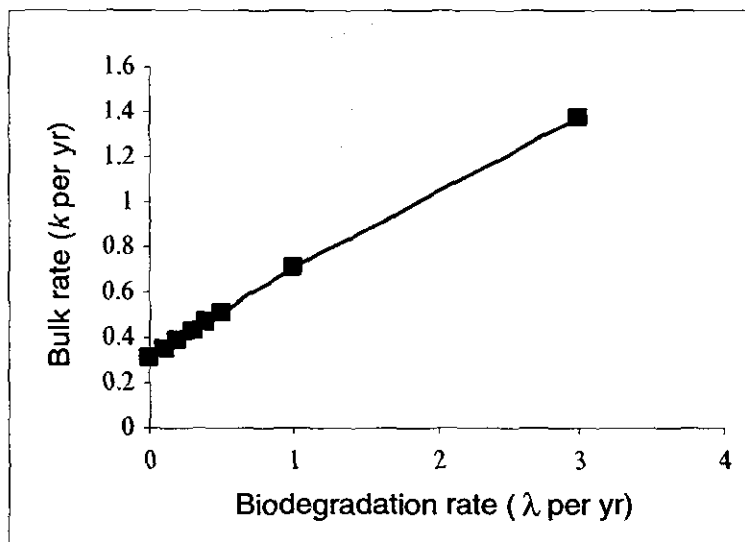
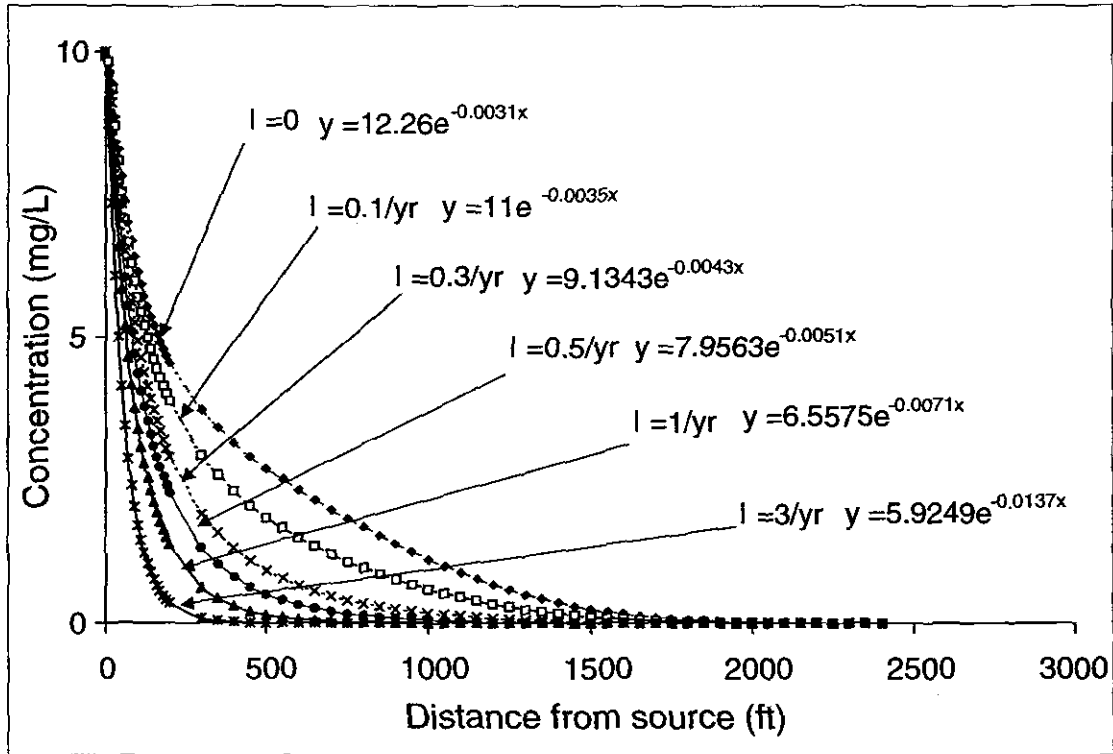
Bulk Attenuation Rate (k) as a Function of Sorption prior to Equilibrium.

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.



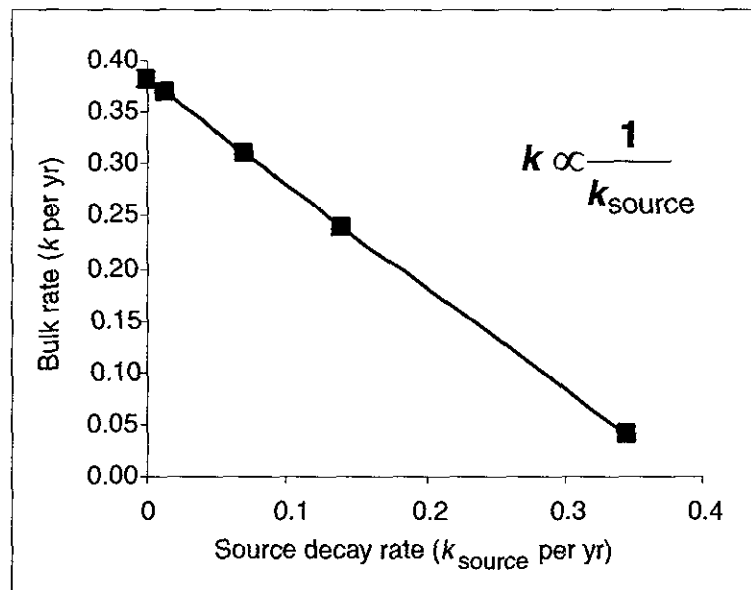
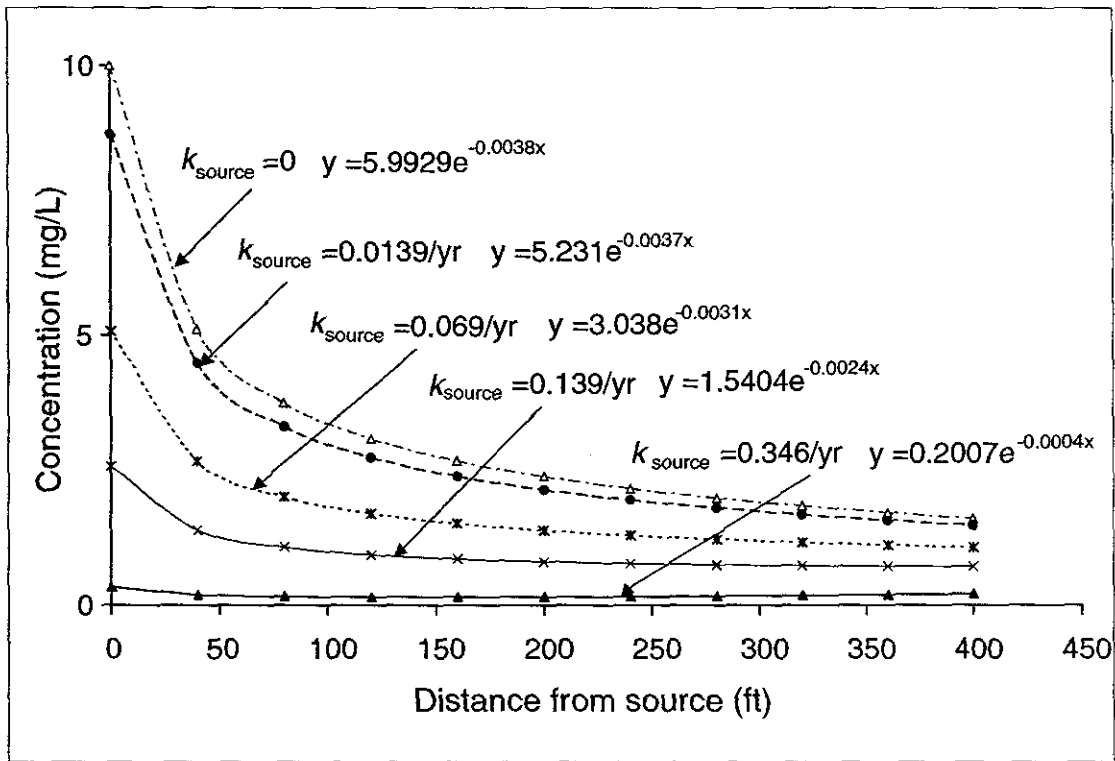
Bulk Attenuation Rate (k) as a Function of Biodegradation Rate (λ)

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.



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.

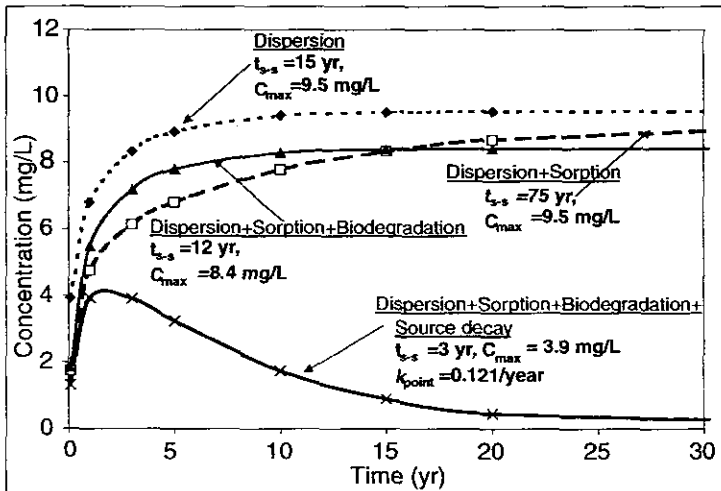
DATA: The parameters assumed for this example are as follows:

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

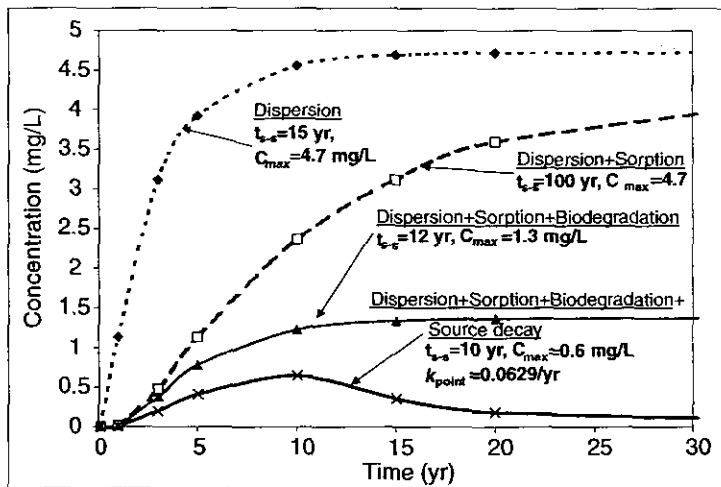
CALCULATION: Four different scenarios were considered to estimate the effect of the different parameters on the overall attenuation rate: 1) the only process acting at the plume is dispersion ($\alpha_x = 100$ ft); 2) previous scenario plus the effect of sorption ($R=5$); 3) dispersion, sorption, and biodegradation ($\lambda=0.2$ 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.

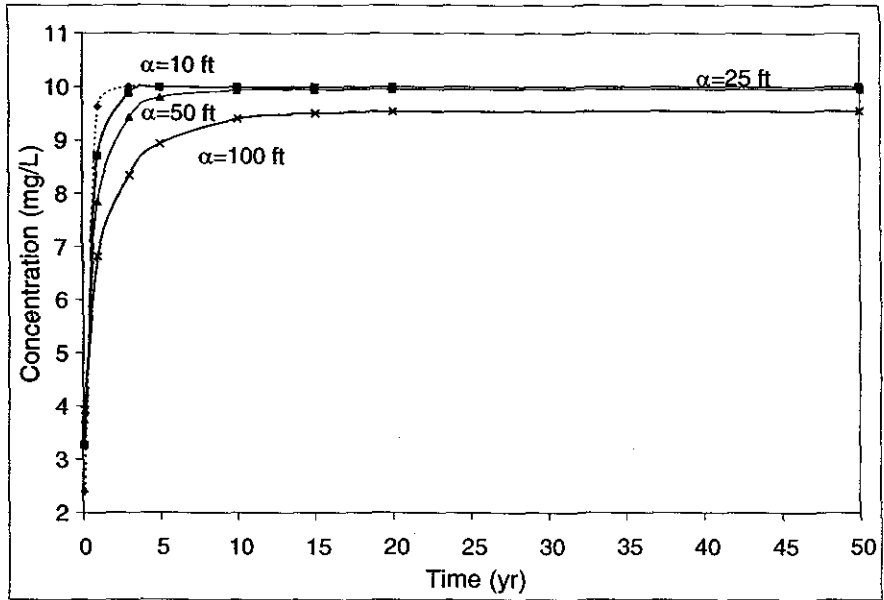


Downgradient location

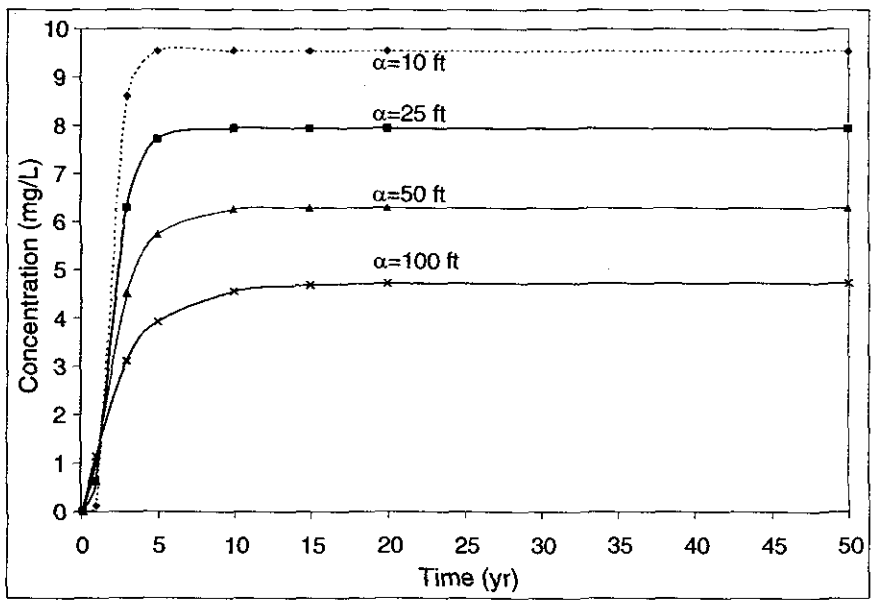
This example illustrates the impacts of the various attenuation processes on the maximum concentrations observed at different locations within a plume. It can be inferred that the more processes present at a given site, the lower the maximum concentration observed. The effect of individual parameters on the Concentration vs. Time profiles is discussed below.

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.



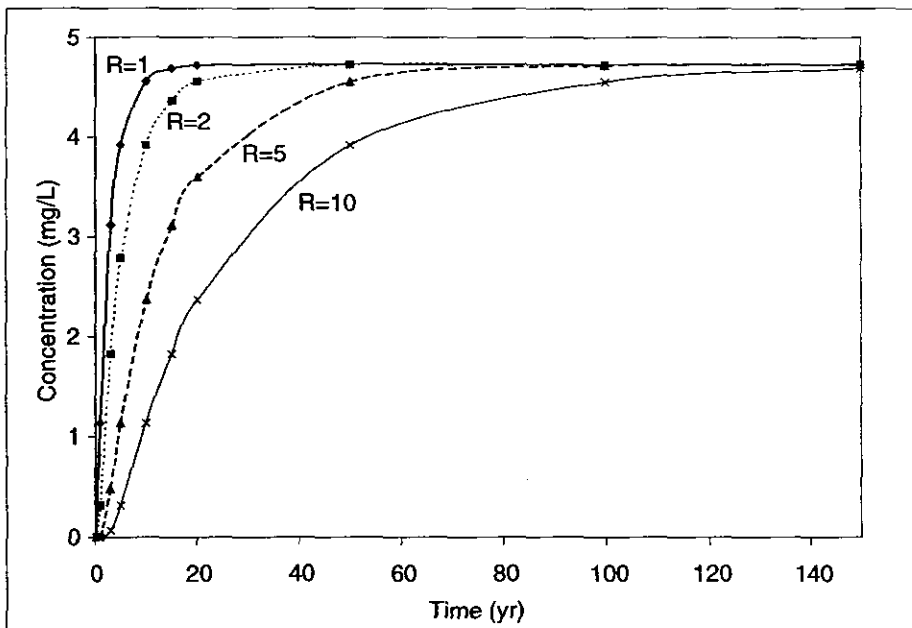
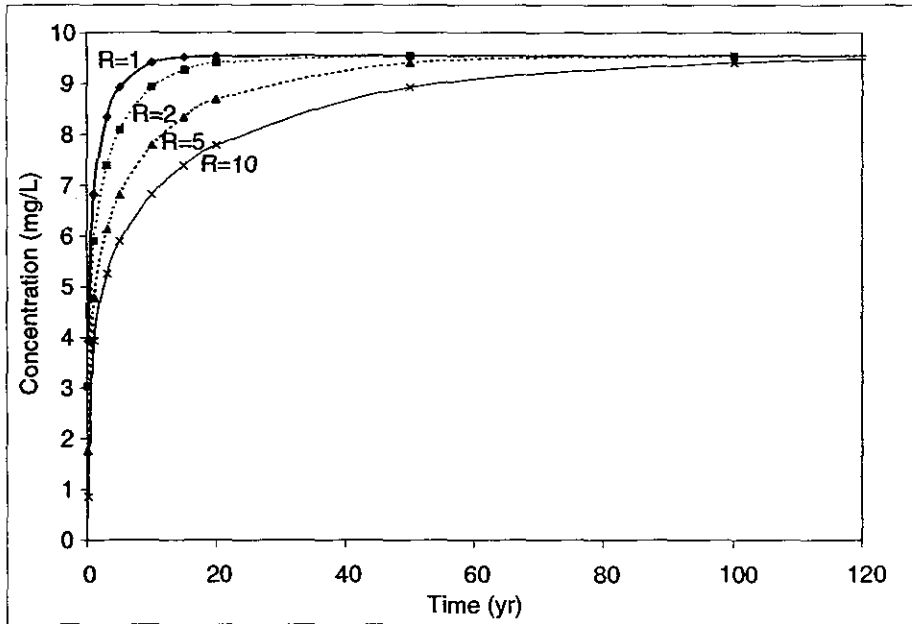
Near source location



Downgradient location

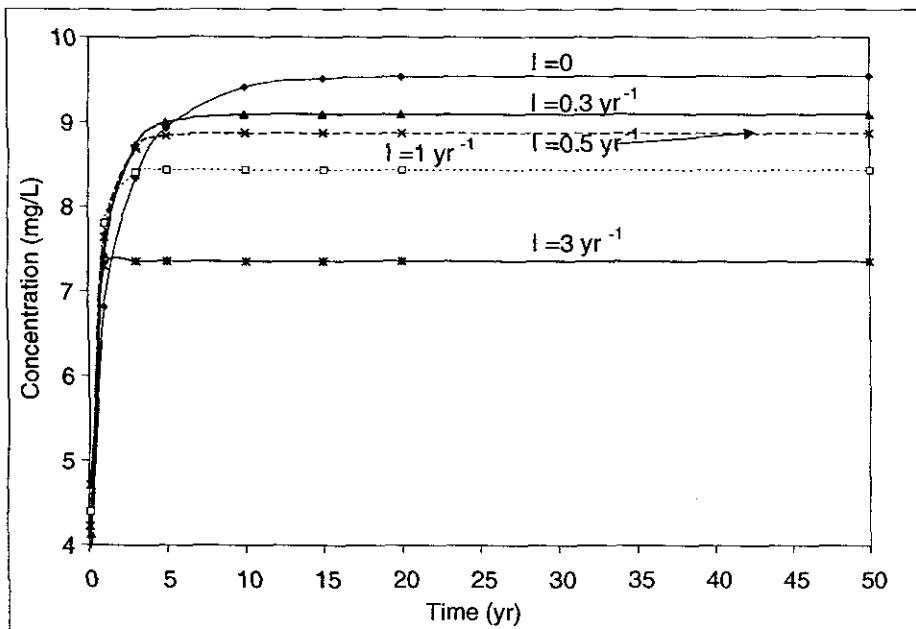
Effect of Sorption on Concentration vs. Time Profiles

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.)

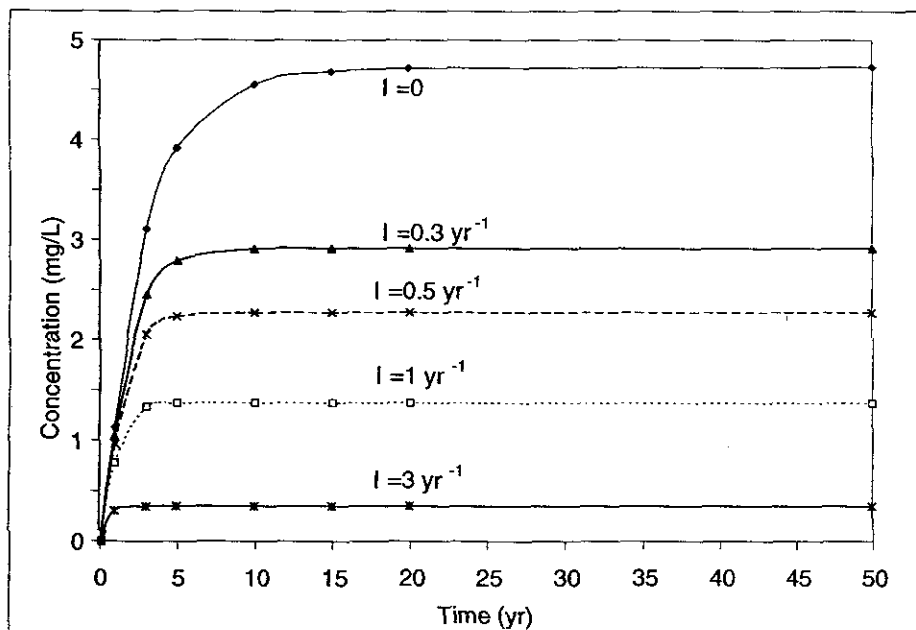


Effect of Biodegradation (λ) on Concentration vs. Time Profiles

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.)



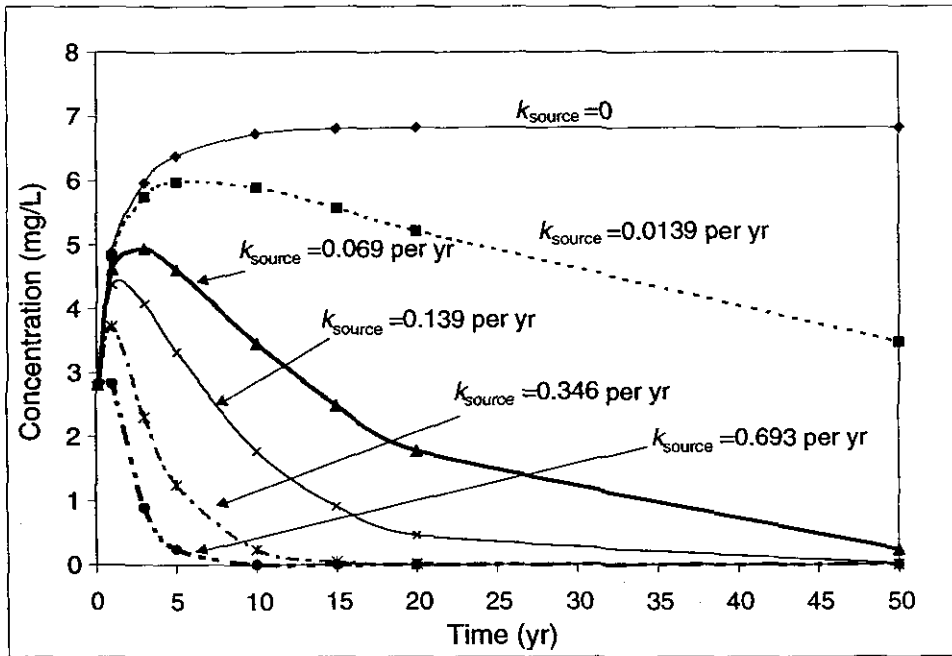
Near source location



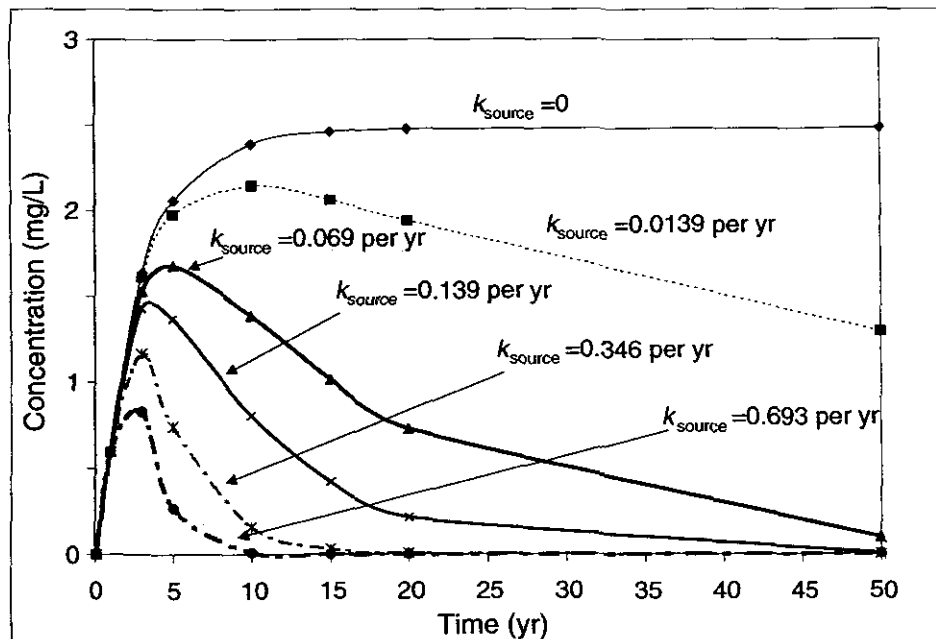
Downgradient location

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.)



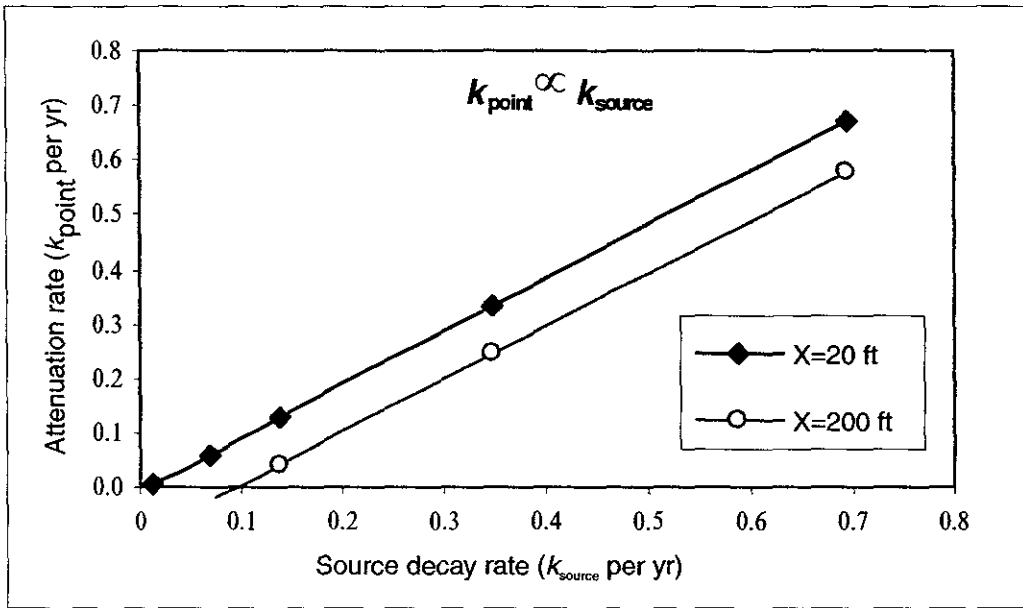
Near source location



Downgradient location

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.



References

- American Society for Testing and Materials, 1998. Standard Guide for Remediation of Ground Water by Natural Attenuation at Petroleum Release Sites. E 1943-98, West Conshohocken, PA. www.astm.org
- Aziz, C.E., C.J. Newell, J.R. Gonzales, P.E. Haas, T.P. Clement, and Y. Sun, 2000. BIOCHLOR Natural Attenuation Decision Support System, User's Manual Version 1.1, U.S. EPA, Office of Research and Development, EPA/600/R-00/008, Washington D.C., www.epa.gov/ada/csmos/models.html
- Borden, R.C., R.A. Daniel, L.E. LeBrun IV, and C.W. Davis, 1997. Intrinsic Biodegradation of MTBE and BTEX in a Gasoline-Contaminated Aquifer. *Water Resour. Res.* 33(5):1105-1115.
- Budge, T., S. Young, and J. Weaver. 2003. Rate-Constant Estimation Software (RaCES) for Extracting Biodegradation Rates from Field Data. Available in 2003 from Jim Weaver at weaver.jim@epa.gov, Later in 2003 the software will be available at <http://www.epa.gov/athens/onsite/index.html>, and <http://www.epa.gov/ceampubl/gwater/index.htm>
- Buscheck, T.E., and C.M. Alcantar, 1995. "Regression Techniques and Analytical Solutions to Demonstrate Intrinsic Bioremediation." In, *Proceedings of the 1995 Battelle International Conference on In-Situ and On Site Bioreclamation*, R. E. Hinchee and R. F. Olfenbuttel eds., Battelle Memorial Institute, Butterworth-Heinemann, Boston, MA.
- Dupont, R.R., C. J. Bruell, D. C. Downey, S. G. Huling, M. C. Marley, R. D. Norris, B. Pivetz, 1998. Innovative site remediation technology, design and application. *Bioremediation*. American Academy of Environmental Engineers, Annapolis, MD. 450 pp.
- Einarson, M.D. and D.M. Mackay, 2001. Predicting Impacts of Groundwater Contamination. *Environ. Sci. Technol.* 35(3):66A-73A.
- Hyman, M., and R.R. Dupont, 2001. Groundwater and soil remediation: process design and cost estimating of proven technologies. American Society of Civil Engineers Press, Reston, VA. 517 pp.
- Kan, A.T., G. Fu, M. Hunter, W. Chen, C.H. Ward, and M.B. Tomson, 1998. "Irreversible Sorption of Neutral Hydrocarbons to Sediments: Experimental Observations and Model Predictions," *Environ. Sci. Technol.*, 32: 892-902.
- Kolhatkar, R., J. Wilson, and L.E. Dunlap. 2000. Evaluating Natural Biodegradation of MTBE at Multiple UST Sites. *Proceedings of the Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Remediation Conference*, API, NGWA, STEP Conference and Exposition, Anaheim, CA, November 15-17, 2000, pp. 32-49.
- Mace, R.E., R.S. Fisher, D.M. Welch, and S.P. Parra, 1997. Extent, Mass, and Duration of Hydrocarbon Plumes from Leaking Petroleum Storage Tank Sites in Texas, Bureau of Economic Geology, University of Texas, Geologic Circular 97-1, Austin, Texas, 1997.
- New Jersey Department of Environmental Protection, 1998. Final Guidance on Designation of Classification Exception Areas, www.state.nj.us/dep/srp/dl/ceaguid2.pdf
- Newell, C.J., and J.A. Connor, 1998. Characteristics of Dissolved Hydrocarbon Plumes: Results of Four Studies, American Petroleum Institute, Washington D.C., December, 1998. www.gsi-net.com
- Newell, C.J., S.K. Farhat, P.C. de Blanc, and J.R. Gonzales, 2002. BIOSOURCE Source Attenuation Decision Support System and Database," Air Force Center for Environmental Excellence, Brooks AFB, TX, in review.
- Newell, C.J., R.K. McLeod, and J. Gonzales, 1996. BIOSCREEN Natural Attenuation Decision Support System, EPA/600/R-96/087, August, 1996. www.epa.gov/ada/csmos/models.html
- Newell, C.J., L.P. Hopkins, and P.B. Bedient, 1990. "A Hydrogeologic Database for Ground Water Modeling." *Ground Water*, 28(5): 703-714.
- Peargin, T.R., 2002. Relative Depletion Rates of MTBE, Benzene, and Xylene from Smear Zone Non-Aqueous Phase Liquid. In *Bioremediation of MTBE, Alcohols, and Ethers*. Editors V.S. Magar, J.T. Gibbs, K.T. O'Reilly, M.R. Hyman, and A. Leeson. *Proceedings of the Sixth International In Situ and On-Site Bioremediation Symposium*. San Diego, California, June 4-7, 2001. Battelle Press. Pages 67 to 74.
- Reid, J. B., and Reisinger, H. J. 1999. Comparative MtBE versus Benzene Plume Length Behavior BP Oil Company Florida Facilities. Prepared by Integrated Sciences & Technology, Marietta, Georgia for BP Oil Company, Cleveland, Ohio.
- Remediation Technologies Development Forum, 1997. Natural Attenuation of Chlorinated Solvents in Groundwater Seminar, RTDF, www.dep.state.pa.us/dep/deputate/airwaste/wm/remserv/biotreat/P_Pman.pdf.
- Rifai, H.S., R. C. Borden, J. T. Wilson and C. H. Ward. (1995). Intrinsic bioattenuation for subsurface restoration, *Intrinsic Bioremediation*, R. E. Hinchee, J.T. Wilson, and D.C. Downey, eds., Battelle Memorial Institute, Columbus, OH, 1-29.
- Rifai, H. S., and C.J. Newell, 2002. Estimating First Order Decay Constants for Petroleum Hydrocarbon Biodegradation in Groundwater, American Petroleum Institute, Soil/Groundwater Technical Task Force, Washington, DC.
- Rice, D.W., R.D. Grose, J.C. Michaelsen, B.P. Dooher, D.H. MacQueen, S.J. Cullen, W.E. Kastenber, L.G. Everett, and M.A. Marino, 1995. California Leaking Underground Fuel Tank (LUFT) Historical Case Analysis, California Environmental Protection Department, November 16, 1995.
- Semprini, L., P.K. Kitanidis, D.H. Kampbell, and J.T. Wilson, 1995. Anaerobic Transformation of Chlorinated Aliphatic Hydrocarbons in a Sand Aquifer Based on Spatial Chemical Distributions. *Water Resour. Res.* 31(4):1051-1062.
- Suarez, M. P. and H. S. Rifai, 1999. Biodegradation Rates for Fuel Hydrocarbons and Chlorinated Solvents in Groundwater, *Bioremediation J.*, 3(4):337 - 362, 1999.
- U.S. Environmental Protection Agency, 1998a. Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater, EPA/600/R/128, Washington D.C., Sept. 1998. www.epa.gov/swrust1/oswermna/mna_epas.htm
- U.S. Environmental Protection Agency, 1998b. Seminar Series on Monitored Natural Attenuation for Ground Water, EPA/625/K-98/001, Washington, D.C., September 1998. www.epa.gov/swrust1/oswermna/mna_epas.htm
- U.S. Environmental Protection Agency, 1999. Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites, Office of Solid Waste and Emergency Response (OSWER), Directive 9200.4-17P, Final Draft, Washington, D.C., April 21, 1999. www.epa.gov/swrust1/oswermna/mna_epas.htm

- Wiedemeier, T. H., H.S. Rifai, C. J. Newell, and J. T. Wilson, 1999. *Natural Attenuation of Fuel Hydrocarbons and Chlorinated Solvents in the Subsurface*, John Wiley and Sons, NY, 1999. www.gsi-net.com
- Wiedemeier, T.H., J.T. Wilson, D.H. Kampbell, R.N. Miller, and J.E. Hansen, 1995. Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater (Revision 0), Air Force Center for Environmental Excellence, Brooks AFB, TX, November 1995.
- Wilson, J.T., J.S. Cho, B.H. Wilson, and J.A. Vardy, 2000, Natural Attenuation of MTBE in the Subsurface under Methanogenic Conditions, EPA/600/R-00/006, www.epa.gov/ada/publications.html.
- Wilson, J.T., and R. Kolhatkar. 2002. Role of Natural Attenuation in Life Cycle of MTBE Plumes. *J. Environ. Eng.*, 128(9):876-882.
- Wisconsin Department of Natural Resources, 1999. Interim Guidance on Natural Attenuation for Petroleum Releases, PUBL-RR-614, Wisconsin DNR, Bureau for Remediation and Redevelopment.



United States
Environmental Protection
Agency

National Risk Management
Research Laboratory
Cincinnati, OH 45268

Official Business
Penalty for Private Use
\$300

EPA/540/S-02/500
November 2002

Please make all necessary changes on the below label,
detach or copy, and return to the address in the upper
left-hand corner.

If you do not wish to receive these reports CHECK HERE :
detach, or copy this cover, and return to the address in the
upper left-hand corner.

PRESORTED STANDARD
POSTAGE & FEES PAID
EPA
PERMIT No. G-35