Guidelines to Determine Site-Specific Parameters for Modeling the Fate and Transport of Monoaromatic Hydrocarbons in Groundwater

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Scott Scheidel, Administrator

IOWA COMPREHENSIVE PETROLEUM UNDERGROUND STORAGE TANK FUND BOARD

AON Risk Services, Inc.

2700 Westown Parkway, Suite 320

West Des Moines, IA 50266

by:

Nanh Lovanh[1], You-Kuan Zhang[2], Richard C. Heathcote[3], and Pedro J.J. Alvarez[1]*

The University of Iowa

[1] Department of Civil and Environmental Engineering and

[2] Iowa Institute of Hydraulic Research

Iowa City, IA 52242-1527

[3] Iowa Department of Justice

Des Moines, IA 50319

TEL: (319) 335-5065

FAX: (319) 335-5660

e-mail: pedro-alvarez@uiowa.edu

* Corresponding author

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INTRODUCTION

General Background

Monoaromatic hydrocarbons such as benzene, toluene, ethylbenzene, and the three isomers of xylene (BTEX) are ground water pollutants commonly associated with petroleum product releases (see Appendix A for physical and chemical properties of these compounds). All six BTEX compounds are depressants to the central nervous system, and chronic benzene exposure can cause leukemia (Federal register, 1985). Thus, contamination of potential drinking water sources by BTEX represents a serious threat to public health. To put the magnitude of this problem in perspective, 370,000 fuel releases from leaking underground storage tanks (LUST) have been confirmed in the U.S. (EPA, 1998). The actual number of tank releases could be as high as 600,000 (Flatham, *et al.*, 1993). In Iowa, 3668 LUST sites are currently active in the Department of Natural Resources files, and 1,378 of these sites are classified as high-risk (Jim Humeston, personal communication, 1999).

Resource allocation considerations have motivated a recent paradigm shift in Iowa and across the U.S. towards risk-based corrective action--RBCA (ASTM, 1994). Because the RBCA paradigm involves trading-off the costs of environmental cleanup for demonstration of actual health and ecological risk from petroleum contamination, accurate risk assessments are critical if the public interest in environmental protection is to be satisfied.

Adoption of RBCA methodology for assessing petroleum contamination in Iowa has placed responsibility heavily on ground water professionals to perform the three-tiered site characterization and risk assessment algorithm accurately, economically, and expeditiously. The procedures for tier 1 and tier-2 assessments are set out in minute detail by IDNR in rules (567 Iowa Admin. Code, Chapter 135) and guidance documents (IDNR, 1996 and 1998). The petroleum contaminated sites that fall through tier 1 and tier-2 assessments and remain in need of corrective action require a much more extensive base of hydrogeological data to evaluate at tier-3. Further, it is sound economical, engineering, and environmental protection policy to know the site-specific hydrogeological parameters as accurately as possible. This document is a compilation of techniques useful in determining the parameters necessary for site characterization in tier-3, and for remediation system design.

Tier-3 assessment is an optional step when tier-2 modeling of a site shows contaminant pathways to at-risk receptors could result in exposure at concentrations that exceed regulatory thresholds. The tier-3 effort might involve merely determining a few additional facts, such as construction detail of an apparently threatened drinking water well, to show the well and aquifer are not actually threatened. Alternatively, the tier-3 effort might be large scale, such as gathering site-specific data sufficient to model fate and transport of chemicals of concern by numerical methods (e.g. Visual MODFLOW-MT3D). Beyond tier-3, a site necessarily goes either into remediation or monitoring for eventual closure. The decision as to whether a remediation effort needs to be active or can be passive in varying degrees - relying on natural attenuation and monitoring, perhaps with stimulation of the natural biota - must be informed by knowledge of many of the same site-specific parameters that support accurate fate and transport modeling.

Certain high-risk sites might be amenable to the use of monitored natural attenuation (MNA) or intrinsic bioremediation, in conjunction with (or instead of) more aggressive corrective action. In fact, nationwide, an increase in the use of intrinsic bioremediation and monitored natural attenuation (MNA) to manage BTEX contamination has been stimulated by the RBCA approach to manage residual BTEX contamination. Within this context, MNA can be defined *as the combination of natural biological, chemical and physical processes that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of the contaminants (e.g., intrinsic bioremediation, dispersion, dilution, sorption, and volatilization).*

Under the Iowa RBCA rules, sites that might be candidates for MNA are those that are high risk because contaminant concentrations exceed the tier-2 site-specific target level (SSTL) at some points between the source and the receptor, but concentrations near the receptor are below the SSTL. The SSTL is represented graphically as a line that shows "acceptable" chemical concentrations between source and receptor (IDNR, 1998, p. 52). Sites with an expanding plume and sample data exceeding SSTL at the receptor might also be candidates for MNA if used in conjunction with active remediation. In either case, it is the responsibility of the ground water professional to assess a site adequately to justify this approach to corrective action.

MNA is typically used in conjunction with active remediation measures (e.g., source control) or as a follow-up to such measures. The success of natural attenuation as a remedial option depends on the following: 1) adequate site characterization; 2) a long-term monitoring plan consistent with the level of knowledge regarding subsurface conditions at the site; 3) evaluation and (if needed) control of the contaminant source; and 4) a reasonable time frame to achieve the remedial objectives.

An extensive investment in site characterization and mathematical modeling is often necessary to demonstrate the existence of natural attenuation at a particular site. Mathematical fate-and-transport models can be very useful in the following ways: 1) to determine if intrinsic bioremediation is occurring at a site; 2) to predict the future extent and concentrations of a dissolved contaminant plume; and 3) to assess the potential for downgradient receptors to be exposed to contaminant concentrations that exceed regulatory levels. It should be kept in mind, however, that simulation results from an improperly calibrated mathematical model can differ considerably from the actual contaminant behavior. Often, the lack of accuracy from the models is due to the inability to obtain the right model parameter values. Needless to say, every effort should be made to obtain accurate site-specific parameter values to enhance the reliability of the model. In particular, it is very important to define the groundwater flow system accurately and to quantify rates of contaminant degradation, which are the processes that have the greatest influence on model predictions (Alvarez at al., 1998b).

Objective

The objective of this report is to provide guidelines for determining site-specific parameters to model the fate and transport of dissolved groundwater pollutants. Ground water professionals will find this report helpful in cases where tier-3 assessments need to be conducted, and when additional site characterization is required to inform a choice about corrective action or remediation system design. This report will emphasize modeling the fate and transport of benzene. This decision is based on the facts that benzene is the most toxic of the soluble components of gasoline, is more mobile than the other aromatic hydrocarbons, and is subject to the strictest cleanup standards because of its carcinogenic properties. Thus, benzene concentrations often determine the need for remedial action at LUST sites. Nevertheless, the fundamental principles and procedures discussed herein are applicable to other groundwater contaminants commonly associated with petroleum product releases.

THEORETICAL BACKGROUND

Most fate-and-transport models are based on mass balances that incorporate processes such as advection, dispersion, chemical reactions, and biodegradation of the target contaminants as a function of time. Mathematical expression of these processes governing contaminant fate and transport is given by Equation B.1 in Appendix B (Domenico and Schwartz, 1998). Solutions to the governing equation B.1 for the case of a continuous contaminant source and the case of a steady-state plume (time invariant) are given by equations B.2 and B.3, respectively. For a decaying contaminant source (which is more representative of a contaminant source undergoing remediation by either engineered solutions or natural weathering), equation B.2a is also a solution to equation B.1. As in any mathematical representation of nature, it is important that boundary conditions and simplifying assumptions be clearly understood. These qualifications and limitations of the models are also stated in Appendix B.

Equation B.1 is a partial differential equation (in its expanded form). As with many partial differential equations that describe the fate and transport of a contaminant, it can be solved analytically (exact and closed-form solutions) with simplifying assumptions. Under the condition of a continuous source, the analytical solution of equation B.2 is obtained. Therefore, mindful of the overall assumptions in obtaining the solution, equation B.2 is most appropriate when the source (spill or leakage from an underground storage tank) is known to be continuous and the contaminant concentration varies as a function of time at a given sampling point. For a contaminant source undergoing remediation by either engineered solutions or natural weathering, equation B.2a is more appropriate (Wiedemeier et al., 1995a). Here, the transient condition is still applied, however, the source is either being removed or undergoing remediation.

Under steady-state conditions, the contaminant concentration does not change with time and thus the right hand side of Eqn. B.1 is equal to zero. In this case the solution for the steady-state concentration is given by Equation B.3. As the name implies, equation B.3 should be used to model a site where steady-state conditions exist or the contaminant plume has ceased to expand

and reached a constant concentration distribution. The steady-state conditions can be determined by analyzing historical data to make sure the plume is stable through time. For simplicity, the Iowa (Tier-2) steady and declining criteria can be used to determine whether or not a plume has reached a steady-state configuration (567 Iowa Admin. Code, 135.12(6)c).

It should be noted that equations B.2 to B.3 are only the analytical solutions to equation B.1. These analytical solutions are generally limited to steady, uniform flow, and should not be used for groundwater flow or solute transport problems in strongly anisotropic or heterogeneous aquifers. These models should not be applied where pumping systems create a complicated non-uniform flow field. Furthermore, these models should not be applied in fractured or karst aquifers, or where vertical flow gradients affect contaminant transport. It should be kept in mind that analytical models are best utilized for order-of-magnitude estimations, since a number of potentially important processes are treated in the models in an approximate manner or sometimes ignored totally.

Inspection of equations B.2 and B.3 plus knowledge of fundamental contaminant hydrogeological relationships shows there are numerous parameters that must be defined before these models can be employed predictively for a specific site in tier-3 risk assessment. There are four sources from which the necessary hydrogeological parameters are obtained: 1) Routine tier 1 and tier-2 assessment (hydraulic conductivity, gradient, source width, source depth, initial concentration, plume length and width); 2) Additional tier-3 site characterization (fraction of organic carbon in soil, porosity, bulk density, advective velocity, retardation factor, soil texture, vertical profile of plume); 3) Established monitoring history of ground water elevations, gradients, and BTEX concentrations (decay coefficient); and 4) Estimation based on site characterization results and hydrogeological literature (dispersivity coefficients).

The situation generating the contaminant plume of interest is shown diagrammatically in Figure 1, below. The dashed lines emanating from the vertical source area represent an ideal contaminant plume undergoing advection and dispersion at three successive times.

Once the site parameters have been confidently determined, the appropriate analytical model from Appendix B or other literature source can be employed to estimate site-specific risk due to migration of chemicals of concern. These equations can be used to calculate contaminant concentrations at points of interest in a ground water plume. Use of a spreadsheet program such as Excel makes testing of many scenarios for a site possible in a short amount of time. See Appendix C for an example of an Excel solution to a site-specific situation.
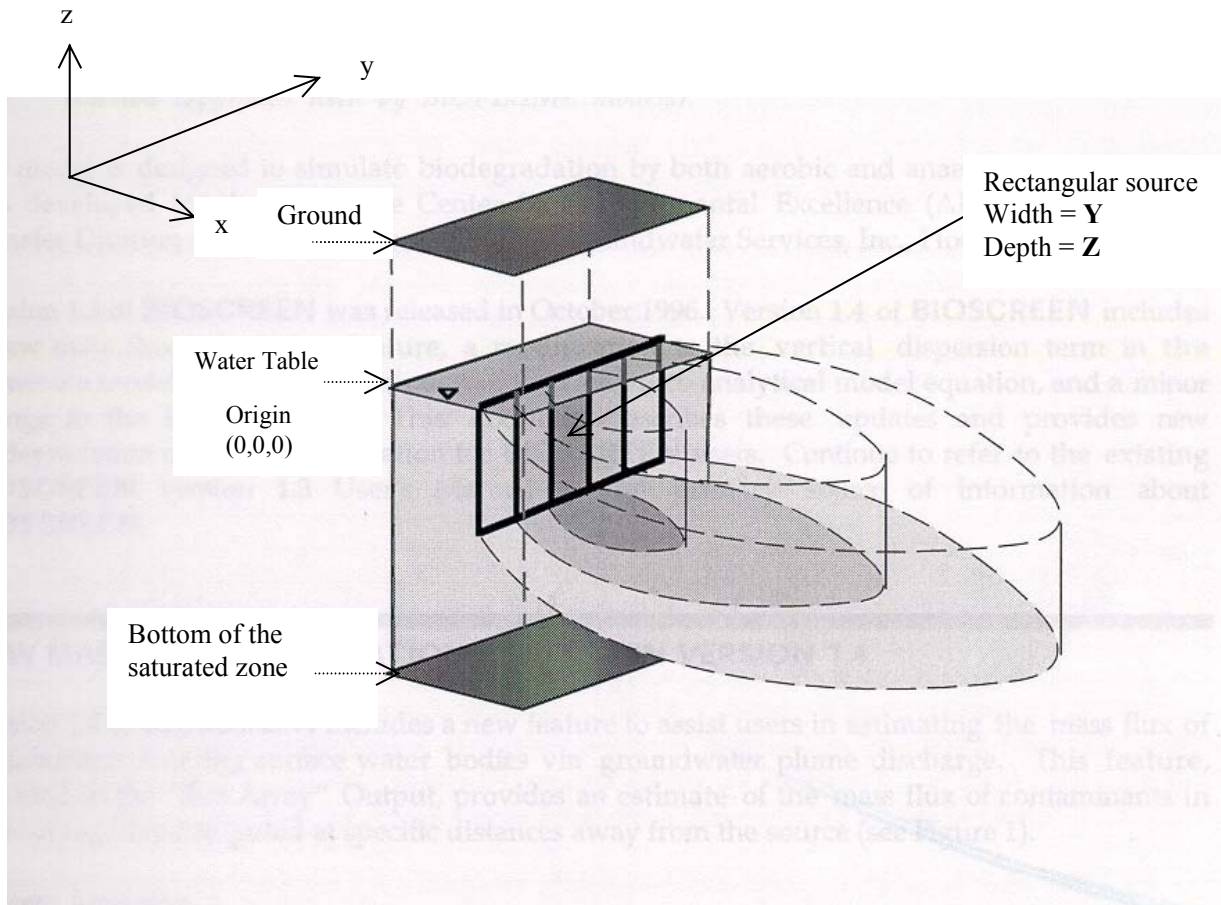
Figure 1. Geometry of the plume model given in Equation B.2 of Appendix B (adapted from Newell et al., 1996)

ESTIMATION OF MODEL PARAMETERS

To obtain site-specific parameters for fate-and transport models, it is important to characterize the geology, hydrology, and chemistry of the site. This requires adequate sampling and measurement, and preparation of lithologic logs, geological maps and cross sections, and potentiometric surface maps. Such information can be used to estimate the values of hydraulic parameters, retardation coefficients, and biodegradation rate coefficients. For contamination from a light nonaqueous-phase liquid (LNAPL) such as gasoline, the rate and amount of partitioning of the chemical of concern (e.g. benzene) from the LNAPL into the groundwater should also be determined to characterize the source concentration (C_0) term. Completion of these tasks allows refinement of the conceptual model and is necessary to support natural attenuation as an appropriate component of remediation. A discussion of selected parameters that describe dissolved BTEX migration and biodegradation rates is provided below, along with guidelines for their determination.

1. Hydraulic Conductivity (K): This parameter is a measure of an aquifer's ability to transmit water and is one of the most important variables governing groundwater flow in aquifers. Hydraulic conductivity has the units of length over time (L/T) and is highly variable. Reported values of K range over 10 orders of magnitude, from 3×10^{-9} to 3×10^{2} m/day (Domenico and Schwartz, 1998) (Table 1). In general, K values for unconsolidated sediments tend to increase with increasing grain size. The velocity of groundwater and dissolved contaminants is directly related to K. Variations in K directly influence the fate and transport of the contaminant by providing preferential migration pathways.

Table 1. Values of hydraulic conductivity for various sediments
(Source: Domenico and Schwartz, 1990).

Materials	Hydraulic Conductivity (m/day)
Glacial till	9×10^{-8} to 2×10^{-1}
Clay	9×10^{-7} to 4×10^{-4}
Silt	9×10^{-5} to 2
Fine sand	2×10^{-2} to 20
Medium sand	8×10^{-2} to 50
Coarse sand	8×10^{-2} to 500
Gravel	30 to 3000
Karstic limestone	9×10^{-2} to 2000
Limestone and dolomite	9×10^{-5} to 0.5
Sandstone	3×10^{-3} to 0.5
Siltstone	9×10^{-7} to 1×10^{-3}
Shale	10^{-9} to 2×10^{-4}

There are several methods to determine K. The choice depends on data availability and the budget of a project. The most common and reliable methods are slug/bail and pumping tests (Butler, 1999, Dawson and Istok, 1991; Kruseman and de Ridder, 1991; Wiedemeier et al., 1995a, 1995b). The Iowa Administrative Code (567 IAC, Chapter 135.2) stipulates that the Bouwer-Rice method (Bouwer and Rice, 1976; Bouwer, 1989) should be used to determine K in saturated soils. The Bouwer-Rice method is one of the techniques used to analyze slug test data in estimating the hydraulic conductivity based on the changing heads produced during the slug test. It is relatively simple and inexpensive. However, it only samples a small area around a well that may or may not be very accurate in determining the hydraulic conductivity for a larger area. Therefore, it is recommended that multiple slug tests be carried out at a given site.   Slug testing of monitoring wells in clay-rich soils requires special procedures to insure that aquifer response and not drainage from the filter pack of the well is being measured (Heathcote and Jones, in prep.). Moreover, there is growing evidence reported in the literature showing that any K determined for an aquifer tends to be larger for larger volumes tested (see Bradbury and Muldoon, 1990; Schulze-Makuch, *et al.*, 1999).

Empirical methods based on grain size distribution may also be used for rough estimations of K when grain size data are available (Freeze and Cherry, 1979; Domenico and Schwartz, 1998). The value of K can also be estimated in the lab using aquifer samples and permeameters with either constant head or falling head (Freeze and Cherry, 1979). Nevertheless, such methods are not accepted by the Iowa Administrative code for modeling purposes.

2. Hydraulic Head (h), Gradient (i) and Groundwater Velocity (u): The total hydraulic head (h) at a given point in the aquifer is the sum of the elevation head (h_z), pressure head (h_p), and the velocity head (h_v) and has a unit of length. The velocity head is usually much smaller than the elevation and pressure heads, and is generally neglected. Thus, the total head is given by

$$h = h_z + h_p \qquad\qquad (2.1a)$$

where the pressure head is related to the fluid pressure (P), the water density (ρ), and the acceleration due to gravity (g), and is given by

$$h_p = P/\rho g \qquad\qquad (2.1b)$$

The total hydraulic head usually changes across a site. The rate of the maximum change in hydraulic head with distance is called hydraulic gradient, which in one dimension is given by

$$i = dh/dx \qquad\qquad (2.2)$$

where the hydraulic gradient (i) is a dimensionless number typically ranging from 0.0001 to 0.05 under natural conditions (Domenico and Schwartz, 1990). To determine the hydraulic gradient accurately, it is necessary to measure groundwater levels in at least three monitoring wells or piezometers at a contaminated site. Because hydraulic gradients can change over a short distance within an aquifer, it is desirable to have as many site-specific groundwater level measurements as possible. Also, seasonal variations in groundwater flow direction can have a substantial influence on contaminant transport. To determine the effect of seasonal variations in

groundwater flow direction, quarterly groundwater level measurements should be taken at the same wells over several years.

The groundwater velocity (u) or the seepage velocity in the direction parallel to groundwater flow is equal to the product of the hydraulic conductivity (K) and the hydraulic gradient (i) divided by the effective porosity (θ_e) (rather than by the total porosity):

$$u = \frac{K\,i}{\theta_e} \qquad\qquad (2.3)$$

According to Domenico and Schwartz (1990), the groundwater velocity typically ranges from 0.0003 to 15 m/day. A survey of 49 LUST sites conducted by Alvarez et al. (1998b) found that the groundwater velocity varied between 0.003 to 1.5 m/day, with a median value of 0.08 m/day and a mean of 0.23 m/day.

To determine ground water flow direction using only three monitor wells, a trigonometry approach can be used. The monitor wells must be placed in a more or less equilateral triangular arrangement to facilitate this. The required data for this method are (1) the spatial locations of the wells, and (2) the total head (water level measurements) at each well (Figure 2). Ground water elevation data from the wells can be used to contour equipotential lines and subsequently construct flow nets (Domenico and Schwartz, 1998). The direction of ground water flow is always from the higher heads to the lower heads and is perpendicular to the head contour (equipotential) lines in isotropic media. The hydraulic gradient can also be calculated using this graphical approach, as the difference between the heads of two contours divided by the shortest distance between the two contours.

Sample calculation based on Figure 2.

Step 1. Well 2 has the intermediate water elevation (head = 7.94 m)
Step 2. Determine Point A (i.e., head = 7.94 m) between wells 1 and 3, by interpolation (see Fig. 2a). The distance between well 1 and well 3 is 43 m. Therefore, Point A is at a distance X from well 1: X = [43(7.96 – 7.94)] / (7.96 – 7.90) = 14.33 m
Step 3. Draw the equipotential line connecting Point A and the intermediate-head well (well 2). This is the line dotted depicted in Figure 2a.
Step 4. Draw a flow vector that is perpendicular to this equipotential line and points towards the well with the lowest head. This vector defines the flow direction.
Step 5. The magnitude of the flow vector can be determined graphically using a map scale. Alternatively, The triangle with vertices at Point A, Point B and well 3 can be determined using basic trigonometric relationships such as the law of sines and law of cosines. In this example, the magnitude of the flow vector (point B to well 3) is denoted by D and is 26.53 m.
Therefore, the hydraulic gradient is equal to: i = (7.94 – 7.90) / (26.53) = 0.0015

Well 1
(head = 7.96 m)

33 m

Well 2
(head = 7.94 m)

43 m

30 m

Well 3
(head = 7.90 m)
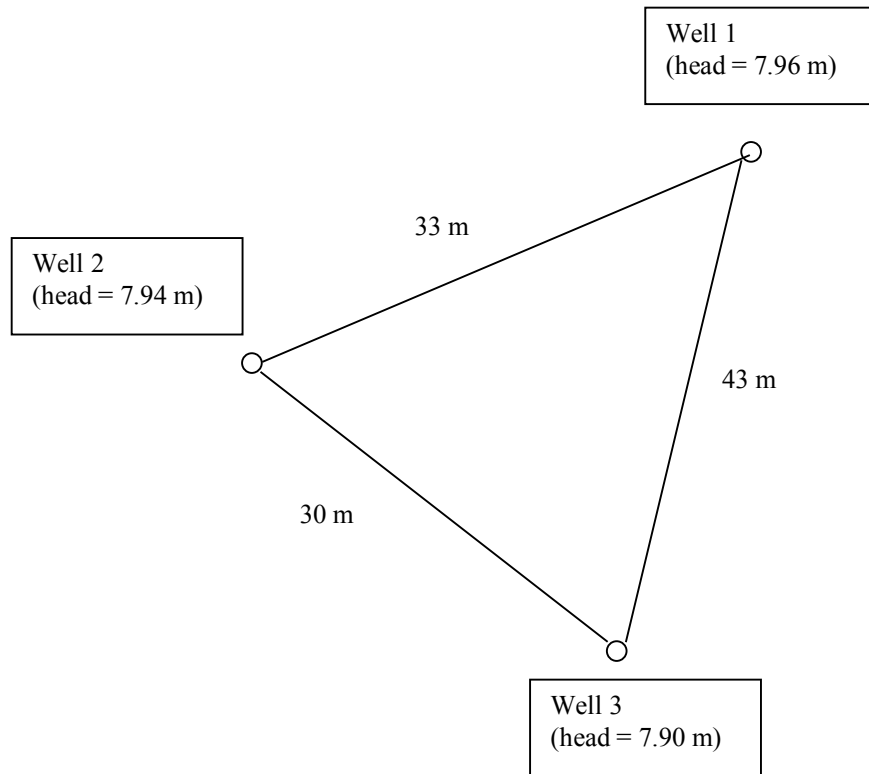
Figure 2. Determination of hydraulic gradient and flow direction by triangulation

Well 1
(head = 7.96 m)

X = 14.33 m

Well 2
(head = 7.94 m)

B   A

90°

Contour line with
Head = 7.94 m

D = 26.53 m

Direction of flow

Well 3
(head = 7.90 m)

Figure 2a. Sketch for determining the direction and gradient of sample in Figure 2

3. Total Porosity (θ_T) and Effective Porosity (θ_e): The total porosity (θ_T) of a porous medium is the volume of voids divided by the total volume of the medium. Effective porosity may be visualized as the connected central passages of a pore network, where fluid flows with negligible resistance from adjacent pore walls, and does not stagnate in dead ends. The effective porosity (θ_e) is the total porosity minus the specific retention (S_r), which is the amount of water that is retained in the medium against the force of gravity. Thus,

$$\theta_e = \theta_T - S_r \tag{3.1}$$

Porosity is a parameter that is commonly selected from the literature, based on the types of aquifer materials (Table 2). Total porosity is easily obtained by a relatively inexpensive geotechnical laboratory method that also estimates the bulk density of a soil sample. Drilling for tier-3 site characterization should include taking at least three core samples for porosity determinations. Tracer tests can then be used to determine effective porosity. For example, an aquifer material core of known volume could be collected and fitted with inlet and outlet valves as a flow-through aquif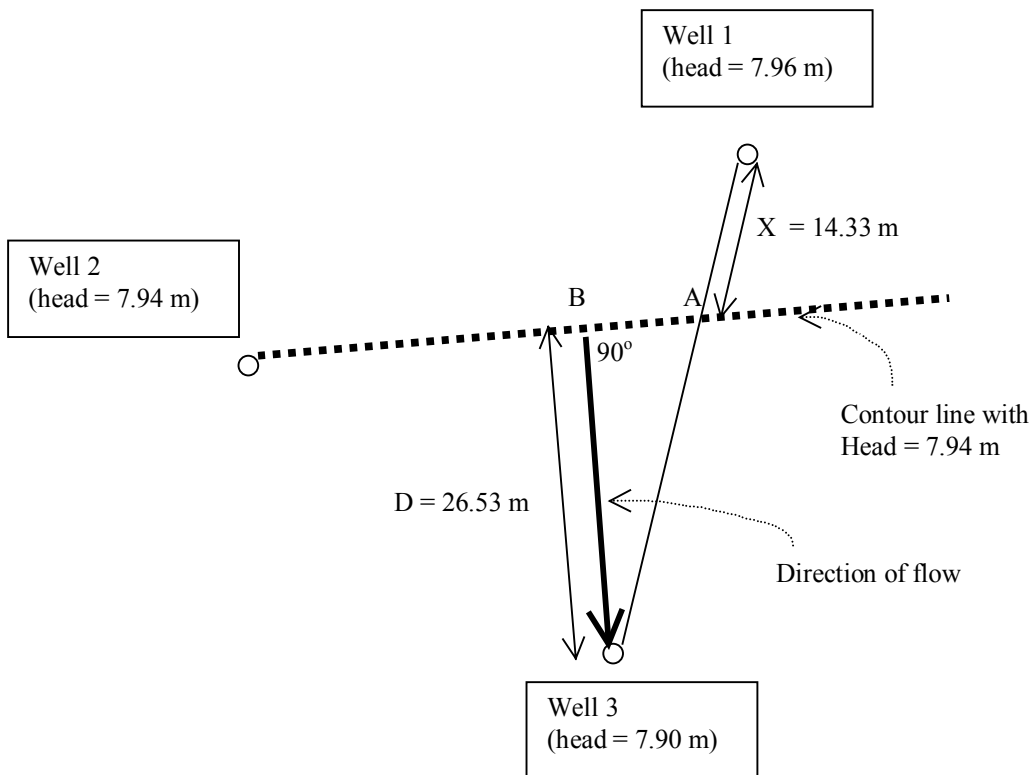er column (Anid et al., 1993; Alvarez et al., 1998a). A bromide solution (50 mg/l) can be continuously injected in an up-flow mode with peristaltic or syringe pumps (e.g., at 2 ml/hr). Effluent bromide concentrations are then monitored (e.g., sampled every 15 minutes) until influent concentration is reached. The mean liquid retention time is estimated as the time required for the effluent bromide concentration to reach 50% of the influent concentration. This time is then multiplied by the flow rate to calculate the pore volume through which water can be freely transmitted. The effective porosity (θ_e) is then calculated as the ratio of this pore volume to the total volume of the core sample.

It should be kept in mind that aquifer materials commonly experience some variability in porosity. Therefore, sensitivity analyses should be performed to determine the effect of varying this parameter on Tier-3 model simulations. Alvarez et al. (1998b) found that using Iowa Tier-2 default parameters, the simulated benzene plume length (defined by 5 ppb contour) increased by about 13% when the value of the total porosity (θ_T) increased by 33% (i.e., from 0.30 to 0.40). This reflects that model simulations are not very sensitive to small errors in porosity (Figure 3), and suggest that little error is introduced by using porosity values from the literature (Table 2).

4. Retardation Coefficient (R): This parameter describes the extent to which the migration of dissolved contaminants can be slowed down by sorption to the aquifer matrix. The degree of retardation depends on both aquifer and contaminant compound properties. The coefficient of retardation is the ratio of the groundwater seepage velocity (u) to the average velocity of a migrating contaminant (v_c). Assuming local linear equilibrium for sorption, the retardation coefficient is given by Equation 4.1 (Freeze and Cherry, 1979).

$$R = u/v_c = 1 + \rho_b K_d / \theta_T \tag{4.1}$$

Table 2. Values of bulk density, total porosity, and effective porosity for common aquifer matrix materials (Source: Domenico and Schwartz, 1990)

Aquifer Materials	Bulk Density ρ_b (g/cm^3)	Total Porosity (θ_T)	Effective Porosity (θ_e)
Iowa default values*	1.86	0.3	0.1
Clay	1 to 2.4	0.34 to 0.60	0.01 to 0.2
Peat	---	-----	0.3 to 0.5
Glacial sediments	1.15 to 2.1	-----	0.05 to 0.2
Sandy clay	---	----	0.03 to 0.2
Silt	---	0.34 to 0.61	0.01 to 0.3
Loess	0.75 to 1.60	---	0.15 to 0.35
Fine sand	1.37 to 1.81	0.26 to 0.53	0.1 to 0.3
Medium sand	1.37 to 1.81	---	0.15 to 0.3
Coarse sand	1.37 to 1.81	0.31 to 0.46	0.2 to 0.35
Gravely sand	1.37 to 1.81	----	0.2 to 0.35
Fine gravel	1.36 to 2.19	0.25 to 0.38	0.2 to 0.35
Medium gravel	1.36 to 2.19	---	0.15 to 0.25
Coarse gravel	1.36 to 2.19	0.24 to 0.36	0.1 to 0.25
Sandstone	1.6 to 2.68	0.05 to 0.3	0.1 to 0.4
Siltstone	----	0.21 to 0.41	0.01 to 0.35
Shale	1.54 to 3.17	0 to 0.1	---
Limestone	1.74 to 2.79	0 to 0.5	0.01 to 0.2
Granite	2.24 to 2.46	----	----
Basalt	2 to 2.7	0.03 to 0.35	----

*The stipulated Iowa values used in the Tier-2 software (Source: Appendix B of 567 Iowa Administrative Code 135).
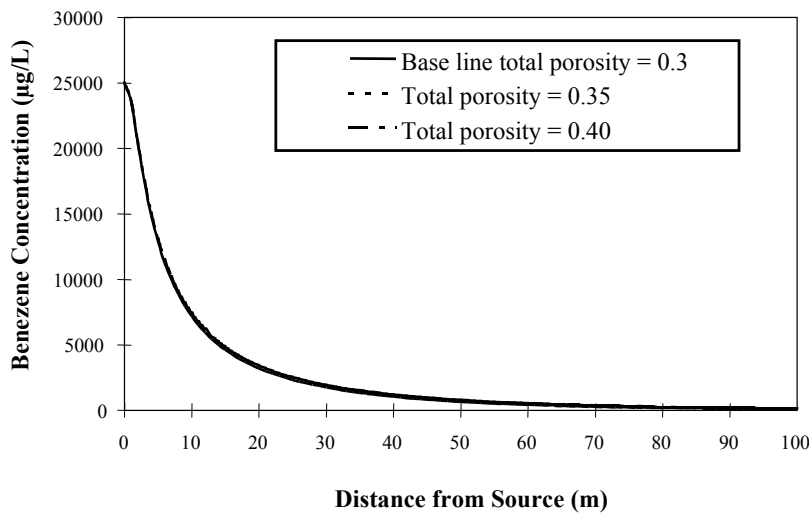
Figure 3. Sensitivity analysis of plume length to the total porosity. Figure depicts simulations for steady-state concentration of benzene along centerline, using Iowa Tier-2 default parameters and different values of the total porosity (Source: Alvarez et al., 1998b). Where ρ_b is the bulk density of the aquifer material, K_d is the distribution coefficient (i.e., the partitioning coefficient between ground water and aquifer material), and θ_T is the total porosity.

It should be pointed out that the retardation coefficient is not necessarily constant, and generally increases over time before reaching a constant value (Roberts et al., 1986).

The retardation of a contaminant relative to the ground water flow has important implications for intrinsic bioremediation. When retardation is occurring, dissolved oxygen and other nutrients and electron acceptors traveling with ground water can sweep over the contaminant plume. This enhances the availability of co-substrates needed for in situ BTEX biodegradation. Also, adsorption of a contaminant to the aquifer matrix results in dilution of the dissolved contaminant plume. Although sorption can decrease the bioavailability of hydrophobic contaminants (Lyman et al., 1992), this is generally not a significant factor that limits BTEX degradation kinetics.

Three site-specific parameters, the total porosity (θ_T), the bulk density of the aquifer material (ρ_b), and the distribution coefficient (K_d), are needed to calculate the retardation coefficient (Eq. 4.1). The total porosity (θ_T) was discussed in Section 3. The bulk density is defined as the ratio between the mass of the solid (M_s) of a sample and the total volume (V_t) of the sample and is related to the particle density (ρ_s) and the total porosity by Equation 4.2

$$\rho_b = M_s / V_t = (1 - \theta_T)\, \rho_s \qquad\qquad (4.2)$$

The distribution coefficient (K_d) can be calculated based the soil adsorption coefficient for soil organic carbon (K_{oc}) and the fraction of soil organic carbon (f_{oc}) as

$$K_d = f_{oc}\, K_{oc} \qquad\qquad (4.3)$$

where K_{oc} is a chemical-specific partition coefficient between soil organic carbon and the aqueous phase. Larger values of K_{oc} indicate greater affinity of contaminants for the organic carbon fraction of soil. The Iowa Administrative Code (567 IAC, Chapter 135, Appendix A) adopted K_{oc} values for different BTEX compounds from the Standard Guide for Remediation of Ground Water by Natural Attenuation at Petroleum Release Sites (ASTM, 1998). These values are listed in Table 3. Smaller partitioning coefficients result in lower retardation factors, which is conducive to faster migration velocity.

For other aromatic hydrocarbons, K_{oc} can be correlated to the octanol-water partitioning coefficient (K_{ow}), which is a measure of compound hydrophobicity (Table 3). A reliable correlation describing this relationship for aromatic hydrocarbons ($r^2 = 0.99$) is given by Schwartzenbach and colleagues (1993)

$$\text{Log } K_{oc} = 1.01\,(\log K_{ow}) - 0.72 \qquad\qquad (4.4)$$

Below is an example calculation of a compound-specific retardation factor.

Example: Calculate the retardation factor for benzene, for an aquifer material with
$f_{oc} = 1\%$, $\theta_T = 0.30$, and bulk density (ρ_b) = 1.86 g/cm^3

> Step 1. Determine value for K_{oc}: Log K_{oc} = 1.58 (Table 3)
>
> Thus, $K_{oc} = 10^{1.58} = 38.02$
>
> Step 2. Calculate value for K_d: $K_d = K_{oc}f_{oc} = 38.02\ (0.01) = 0.38$
>
> Step 3. Calculate value for R_f: $R_f = 1 + ((1.86)(0.38)/0.30) = 3.36$
>
> Thus, in this aquifer material, benzene would travel 3.36 times slower than groundwater.

If K_{oc} had been calculated using Eqn. (4.4) with log K_{ow} = 2.12, the value of K_d would have been 0.26, yielding in turn a (smaller) retardation factor of 2.47. Therefore, K_{oc} values calculated by the method of Schwartzenbach et al. (1993) yield faster contaminant migration velocities and are more conservative than K_{oc} values listed in the Iowa Administrative Code (Table 3).

Table 3. Partitioning Coefficients for different monoaromatic hydrocarbons

Compound	Log K_{oc}[1]	Log K_{ow}[2]
Benzene	1.58	2.12
Toluene	2.13	2.73
Ethylbenzene	1.98	3.15
m-Xylene	2.38	3.20
Trimethylbenzene	---	3.59

[1]Source of soil organic carbon-water partitioning coefficients (K_{oc}): ASTM, 1998.
[2]Source of octanol-water partitioning coefficients (K_{ow}): Howard, 1990.
Additional physical and chemical properties of monoaromatic hydrocarbons are given in Table A-1 in Appendix A.

The value of f_{oc} (which is needed to calculate K_d) must be measured in the lab, using standard techniques such as those described by Nelson and Sommers (1982). A higher content of natural organic carbon (i.e., higher f_{oc}) results in higher adsorption of organic constituents on the aquifer. Typical ranges of f_{oc} are given in Table 4.

The Tier-2 Site Cleanup Report Guidance (IDNR, 1998, p. 35) states: "If the default soil parameter values [θ_T, ρ_B, f_{oc}] are to be replaced with site-specific values, all three soil parameters must be measured and used to calculate the soil target levels. An average of three samples must be used to obtain a site-specific value for each parameter (i.e., a total of nine soil samples must be sent to the laboratory for analysis.) Therefore, samples for each parameter must be collected from three different locations considered representative of site conditions. Additionally, samples must be collected at the same depth and in the same stratigraphy as that of the maximum soil contamination location. Samples for [f_{oc}] determination must be collected from an uncontaminated area. Samples for [ρ_B] and [θ_T] may be collected from within the plume or from an uncontaminated area."

Table 4. Representative values of total organic carbon content in various sediments (Source: Domenico and Schwartz, 1998)

Type of Deposit	Texture	Fraction Organic Carbon (f_{oc})

Iowa default value	Iowa default value	0.01*
Fluvial-Deltaic	Medium sand	0.00053 to 0.0012
Glaciofluvial	Sands and gravels	0.0004 to 0.0007
Glacial (lacustine)	Organic silt and peat	0.10 to 0.25
Back-barrier (marine)	Fine to coarse sand	0.00026 to 0.007
Eolian	Loess (silt)	0.00058 to 0.0016
River sediment	Sand, coarse to fine silt	0.0057 to 0.029

*Value used in Iowa Tier-2 software (Source: Appendix B of 567 Iowa Administrative Code, Chapter 135).

It must be remembered that the retardation factor for a dissolved contaminant characterizes the advective flow of the concentration contour that is 50% of the (constant) source concentration (i.e., $C/C_0 = 0.5$). Because some contaminant molecules migrate further than this contour, the first appearance of a contaminant in low concentrations at some down gradient monitoring well will likely be sooner than one predicts based on the retarded velocity alone.

5. Hydrodynamic dispersion coefficient (D) and dispersivity (α). Dispersion is a process that spreads contaminants out beyond the region they would occupy due to advection alone. Dispersion is important to consider because it allows the solute plume to be diluted by uncontaminated ground water. In addition, dispersion mixes the plume with uncontaminated ground water and replenishes it with nutrients and electron acceptors, such as dissolved oxygen, nitrate, and sulfate. Natural attenuation might be enhanced around plume margins due to dispersive (dilution) effects.

In ground water hydrology, dispersion is traditionally called hydrodynamic dispersion (Bear, 1972) which includes the molecular diffusion and mechanical dispersion. Molecular diffusion is caused by a concentration gradient and can be described with the parameter (D_d). Mechanical dispersion is mixing caused by local variations in velocity around the mean flow velocity, v_x; it is described with the mechanical dispersion coefficient (D'). The hydrodynamic dispersion coefficient (D) is summation of D and D' or

$$D = D_d + D' \qquad (5.1)$$

In three dimensions, the coefficient D' has three components along three perpendicular coordinates (x, y, z), which are assumed to be proportional to three ground water velocity components u_x, u_y and u_z:

$$D'_x = \alpha_x u_x; \qquad D'_y = \alpha_y u_y; \qquad D'_z = \alpha_z u_z; \qquad (5.2)$$

where α_x, α_y, and α_z are the longitudinal dispersivity, the horizontal transverse dispersivity, and the vertical transverse dispersivity, respectively. The longitudinal dispersivity has been found to increase with time or travel distance in a given experiment and to increase with the scale among

different experiments (Gelhar, 1993; Zhang and Neuman, 1990). This has been called the scale effect (Anderson, 1979), which is caused by the large-scale heterogeneity of an aquifer. It is difficult, if not impossible in practice, to determine dispersivities as functions of time. A common practice is to ignore the time-dependent behavior and to use a constant apparent or effective dispersivity.

There are several methods for estimating the apparent longitudinal dispersivity. The simplest method is the so-called Rule of Thumb (Gelhar, 1993). This rule is based on the observation that the longitudinal dispersivity increases with an overall scale or the travel distance (L) of a contaminant from a source, as shown in Figure 4, where a straight line is fitted to the observed values. The slope of this line is 0.1, meaning that the apparent longitudinal dispersivity is one-tenth of L (American Society for Testing and Materials, 1994) or

$$\alpha_x = 0.1 * L \tag{5.3}$$

where L id the average travel distance of the plume. For a continuous source when dispersion occurs only in the x direction, the average traveled distance of a plume is the distance between the source and the advanced front at which the concentration is half of the source concentration ($C/C_0 = 0.5$). However, the average travel distance of the plume cannot be easily determined for the more common case when dispersion occurs in three dimensions. Therefore, L in eq. 5.3 is often represented by the plume length; i.e., the downgradient distance between the source and the contour where the benzene concentration of 5 μg/L, which is the drinking water standard.
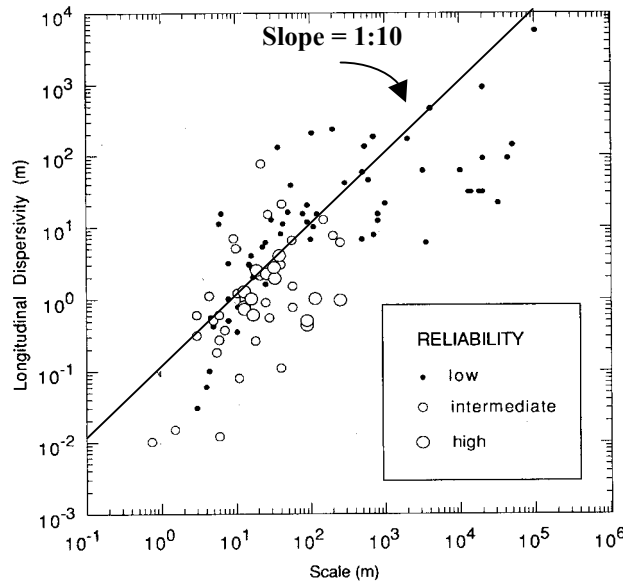

Figure 4. Longitudinal dispersivity as a function of scale (based on Gelhar et al., 1992)
Equation (5.3) is slightly different from that in Tier-2 Site Cleanup Report Guidance, i.e.

$$\alpha_x = 0.1 * x \tag{5.4}$$

where x is the downgradient distance along the principal ground water flow direction. Both formulae incorporate the scale-dependence of the longitudinal dispersivity.

Whereas, eq. (5.4) serves well the conservative intent of tier-2 modeling, at tier-3, or in estimation of MNA effectiveness, eq. (5.3) is recommended for the following reasons. First, analytical solutions to the fate-and-transport governing equation (e.g., eq. (B.2)) cannot be obtained if α_x is a function of x, which makes eq. (5.4) mathematically inconsistent with the Iowa Tier-2 ground water contaminant model. Secondly, field experiments have shown that one could fit tracer data more accurately by using a constant dispersivity value for all points within the plume at a given time (Dieulin et al., 1981; De Marsily, 1986). As the plume spreads, the dispersivity increases with the average traveled distance of all tracer particles rather than with the distance traveled by individual particles. Thirdly, eq. (5.4) predicts that α_x will increase indefinitely with x. However, both theoretical results (Dagan, 1989; Zhang and Neuman, 1990) and field tracer experiments (Mackay et al., 1986; LeBlanc et al., 1991; Boggs et al., 1992) have shown that α_x reaches an asymptotic (constant) value at large time or large scale in most aquifers. This asymptotic value is usually approached after the plume travels a distance between 10 to 50 meters in unconsolidated materials (Dagan, 1984; Neuman and Zhang, 1990; Zhang and Neuman, 1990). In the famous Borden experiment (Mackay et al., 1986; Freyberg, 1986; Sudicky, 1986) the longitudinal dispersivity approached a constant value of about 0.5m after the center of the plume moved 30m from the injection point. The value of dispersivity stayed at this constant value of 0.5m even after the plume center moved from 30m to 100m from the source in the experiment.

Using universal scaling, Neuman (1990) proposed a better scale-dependent, empirical method for estimating α_x:

$$\alpha_x = 0.0175 \ L^{1.46} \qquad (5.5a)$$

for L less than and equal to 100 m and

$$\alpha_x = 0.32 \ L^{0.83} \qquad (5.5b)$$

for L larger than 100 m.

This approach generally yields more accurate estimations of α_x compared to equations 5.3 and 5.4. Considering the conceptual inconsistencies mentioned above for the formula used currently by the Tier-2 model (i.e., Eqn. (5.4)), it is recommended that equations (5.5a) and (5.5b) be used instead of equations (5.3) or (5.4).

Other empirical approaches have been proposed that have the potential to yield more accurate estimations of α_x. Some of these methods, however, have extensive data requirements, and the additional cost associated with obtaining these data is not always justified in terms of improved simulation accuracy. Examples of these approaches are given below.

The apparent dispersivity can be related to geostatistical parameters of hydraulic conductivity (Dagan, 1989; Domenico and Schwartz, 1990).

$$\alpha_x = \sigma^2_Y * \gamma_Y \qquad (5.6)$$

where σ^2_Y is the variance of log-transformed hydraulic conductivity (Y = log K) and γ_Y is the correlation length of Y. These two parameters can be calculated based on a number of Y values (Domenico and Schwartz, 1990). When multiple values of K are not available, one may consider the values of the variance of the natural logarithm of hydraulic conductivity or transmissivity in Table 5. For the correlation scale (γ_Y), Gelhar (1993) suggests using one-tenth of the overall scale or one-tenth of the plume length, i.e.,

$$\gamma_Y = 0.1 * L \qquad (5.7)$$

Table 5. Typical values of the variance of the natural logarithm of hydraulic conductivity for various geological formation (Revised from Gelhar 1993)

Medium	Variance of log-transformed hydraulic conductivity (dimensionless), σ^2_Y
Alluvium	0.2 – 1.5
Fluvium	0.8 – 4.4
Glacials	0.3 – 0.6
Limestone	5.25
Sandstone	0.4 – 4.8

In summary, dispersion of a contaminant in a heterogeneous aquifer is a complex process and is mainly caused by ground water velocity variations at different scales. This variation is, in turn affected by variations of hydraulic conductivity. Without detailed knowledge of these variations, which is usually the case, accurate calculation of the dispersion coefficients is difficult and one has to rely on rough estimates (e.g., equations 5.3 to 5.5). It is recommended that Neuman's (1990) method (equation 5.5) should be used when the hydraulic conductivity data is limited. The geostatistical method (equation 5.6) may be used to improve the estimate for the longitudinal dispersivity when multiple measurements of hydraulic conductivity at different points in a site are available.

The transverse dispersivity (α_y) is commonly set to be equal to 30% of the longitudinal dispersivity, and the vertical dispersivity (α_z) is taken to be 5% of the longitudinal dispersivity (American Society for Testing and Materials, 1994). The Iowa Administrative Code stipulates that the transverse dispersivity is equal to 33% of the longitudinal dispersivity and the vertical dispersivity is equal to 5% of the longitudinal dispersivity.

6. Biodegradation rate coefficient (λ).

General Background.

This is the parameter that describes the rate at which a contaminant is being degraded. The degradation rate usually follows a first-order decay regime with respect to the contaminant concentration (C):

$$\frac{dC}{dt} = -\lambda C \tag{6.1}$$

In describing an ideal, completely mixed system with no inflow or outflow of mass (a batch experiment), Equation (6.1) can be integrated to yield:

$$\frac{C}{Co} = e^{-\lambda t} \tag{6.2}$$

where Co is the initial concentration. Thus, in a completely mixed batch system, a plot of ln(C) versus time should give a straight line, and λ can be determined as the slope of this line. Equation (6.2) can be rearranged as

$$t = \frac{\ln\left[Co/C\right]}{\lambda} \tag{6.3}$$

The half-life ($t_{1/2}$) of the contaminant, which is defined as the time required to reduce its concentration by one-half, is given by

$$t_{1/2} = \frac{\ln[2]}{\lambda} \tag{6.4}$$

It should be emphasized that these equations apply only to batch, completely mixed systems, where dilution and advection are not factors that influence BTEX concentrations. Because aquifers are open systems subject to dilution and advection, other approaches that incorporate these processes must be used to determine λ. Field techniques for such determinations are discussed later in this report.

The first-order kinetic assumption is usually appropriate to describe the kinetics of BTEX biodegradation in aquifers. This is mainly due to mass transfer limitations in porous media as the contaminants diffuse from the ground water into the microorganisms, which are predominantly attached to the aquifer material (Simoni et al., 1999). In addition, a decrease in BTEX concentrations to levels that are below the corresponding Monod's half saturation coefficient (Ks) contributes to first-order kinetics (Alvarez et al., 1991). It should be pointed out that when mass transport is not rate-limiting, λ can be explained in terms of Monod parameters.

Specifically, when the contaminant concentration is relatively low, we can ignore C in the denominator and Monod's equation reduces to a linear equation:

$$\frac{dC}{dt} = -\frac{kXC}{K_S + C} = -\left(\frac{kX}{K_S}\right)C \quad \text{(when C<<K}_s\text{)} \qquad (6.5)$$

A comparison of equations 6.1 and 6.5 therefore reveals that

$$\lambda = \frac{kX}{K_S} \qquad (6.6)$$

This theoretical analysis indicates that the value of λ depends on:

a) **k** (the maximum specific substrate utilization rate) which in turn depends primarily on the prevailing electron acceptor conditions, and on the type of microbe present;

b) **K$_s$** (the half-saturation coefficient), which is related to enzyme affinity, bioavailability, and mass transport limitations (Merchuk and Ansejo, 1995); and

c) **X** (the active biomass concentration) which may not be constant, and depends on environmental conditions and aquifer chemistry, including available substrates.

Therefore, λ is not necessarily a constant, but a coefficient that can vary in time and space due to microbial population shifts resulting from changes in aquifer chemistry. This can explain the wide range of λ values that have been observed for benzene at different sites, ranging over several orders of magnitude from 0 to 0.087 day^{-1} (Alvarez et al., 1991, 1998b; Aronson and Howard, 1997; Howard, 1990, Howard et al. 1991; Rifai et al., 1995). Therefore, λ should not be extrapolated from the literature. Rather, considerable care must be exercised in its determination to avoid over-predicting or under-predicting actual biodegradation rates and plume behavior.

Field Methods to determine λ.

There are several different methods to determine site-specific biodegradation rate coefficient, λ. These methods include mass balances, the technique of Buscheck and Alcantar, normalization of BTEX concentrations to those of a recalcitrant hydrocarbon that was present in the initial release, such as trimethylbenzene or tetramethylbenzene, and the use of in situ microcosms. Advantages and disadvantages of such approaches are summarized in Table 6.

Table 6. Common field methods for determining the biodegradation rate coefficient

Methods	Advantages	Disadvantages

Mass Balance	• Direct λ measurement • High accuracy for a pulse release, or for shrinking plumes	• Unreliable for continuous-source, and for steady plumes • Requires extensive amount of time and numerous well clusters screened at different depths • Need to discern other sinks that are not associated with biodegradation process (could overestimate λ)
Buscheck & Alcantar	• Simple analysis • Does not require extensive monitoring	• Applicable only for constant source, steady plume • Need series of wells along the plume centerline • Can overestimate λ since a decrease in contaminant concentration due to horizontal and vertical dispersion is intrinsically attributed to biodegradation
TMB Normalization	• Simple analysis • Can be used for steady and transient plumes	• Need series of wells along the plume centerline • TMB tracer may be degraded which will lead to the underestimation of λ
In situ microcosms	• Simple analysis • Can measure rates in different redox zones of the aquifer	• O_2 could be inadvertently introduced when device is installed or when contaminants are added • Sorption processes confound kinetic interpretation and analysis • Does not incorporate potential interactions between degradation, advective, and dispersive processes

The mass balance approach, described by Chiang et al. (1989), constitutes a rigorous demonstration of natural attenuation. In contaminant in the subsurface is monitored over time by interpolation and integration of monitoring well data. The first-order attenuation this method, an extensive monitoring well network is installed to define the complete vertical and horizontal extent of the dissolved hydrocarbon plume. The total mass of a rate (or the biodegradation rate coefficient) is determined as the percent of contaminant depleted per period of time, usually normalized to a unit of reciprocal days (d^{-1}).

The mathematical relationship is stated in Equation 6.7.

$$\lambda = [(M_o - M)/M_o]/\Delta t \qquad\qquad (6.7)$$

Here, M_o is the initial contaminant mass at $t = 0$, M is the contaminant mass remaining at time t, and Δt is the corresponding elapsed time. In using this technique, one has to take into the account the net influx rate from the contaminant source and other mechanisms (e.g., sorption, volatilization, etc.) which are not part of the actual biodegradation process. This mass balance

technique is a direct and quantitative method of demonstrating natural attenuation. However, the cost associated with the extensive monitoring network required for this approach and the relative complexity of the analyses precludes its application at most sites other than research sites (Chiang et al., 1989). Furthermore, in many cases, dissolved gasoline plumes will reach pseudo-steady state conditions when contaminant concentrations in monitoring wells stabilize (with minor fluctuations) because of the combined effects of contaminant dissolution at the (continuous) source, downgradient transport of the dissolved constituents, and subsequent biodegradation. In this situation the mass balance approach cannot be used to estimate λ since the mass of dissolved contaminant in the aquifer will be relatively constant. Therefore, this approached works best for pulse releases of dissolved phase contaminants.

Another method that is frequently used to determine λ is the technique of Buscheck and Alcantar (1995). This method is based on an analytical solution for one-dimensional, steady-state, contaminant transport that considers advection, longitudinal dispersion, sorption, and first-order biodegradation (Equation 6.8).

$$C(x) = C_o \exp\left\{\left(\frac{x}{2\alpha_x}\right)\left[1 - \left(1 + \frac{4\lambda\alpha_x}{v_c}\right)^{1/2}\right]\right\} \tag{6.8}$$

Buscheck and Alcantar (1995) recognized that contaminant concentrations usually decrease exponentially along the centerline of the plume as the distance from the source increases. This trend is described by eq. (6.8a):

$$C(x) = C_o \exp\left(\frac{-kx}{u}\right) \tag{6.8a}$$

Where k is the decay coefficient, which incorporates biodegradation, dilution, sorption, etc., x is the distance from the source, and x/u is the time it takes groundwater to travel a distance x.

Buscheck and Alcantar (1995) equated equations (6.8) and (6.8a), and solved for λ:

$$\lambda = (v_c/4\alpha_x)\{[1 + 2\alpha_x(k/u)]^2 - 1\} \tag{6.9}$$

where k/u = the negative of the slope of a line obtained from a log-linear plot of the (center-line) contaminant concentration versus distance downgradient along the flow path, and all other terms are as previously defined. Note that if biodegradation is assumed to occur only in the liquid phase (i.e., adsorption of a contaminant removes it from microbial access), the term v_c in Equation 6.9 should be replaced by the ground water seepage velocity, u (ASTM, 1998).

To determine λ using this approach also requires knowledge of the longitudinal dispersivity (α_x) and the contaminant (retarded) velocity (v_c). The following example, based on the field data listed in Table 7, illustrates how to obtain the slope of the regression line from the centerline contaminant concentration versus migration distance (i.e., k/u), and how subsequently to calculate λ.

Example: The following benzene concentrations have been measured in a steady plume at four wells placed along the principal flow (x) direction. Seepage velocity is 0.03 m/d, and dispersivity is estimated to be 7.5 m.

Table 7: Benzene concentrations from four wells placed along the principal flow direction

Distance from source along centerline, x (m)	Benzene concentration, C (µg/l)	ln C
1	4000	8.2940
50	200	5.29831
95	10	2.30258
155	0.2	-1.6094

Step 1. Plot the ln(C) versus x data.
Step 2. Perform a linear regression to obtain the slope (Figure 5). The negative of the slope is the term k/u, needed to solve equation 6.9. In this example, using the regression routine from Excel, $k/u = 0.0645$ m^{-1}
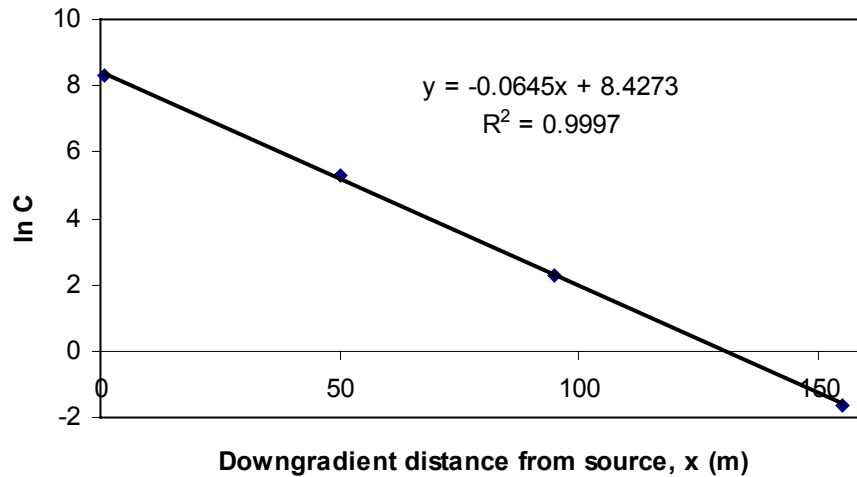

Figure 5. Example of linear regression to determine k/u by the Buscheck & Alcantar method

Step 3. If biodegradation is assumed to occur only in the liquid phase, then the biodegradation rate coefficient can be determined from Eq. 6.9:

$$\lambda = [0.03/(4*7.5)]\{[(1+2*7.5(0.0645)]^2 - 1\} = 0.0029 \text{ day}^{-1}$$

This corresponds to a half-life of ln(2)/0.0029 = 239 days.
The method of Buscheck and Alcantar (1995) requires the plume to be at steady-state and the monitoring wells to be located along the centerline of groundwater flow path. In practice, the monitoring wells are rarely ideally located as required by this technique. Furthermore, steady-state conditions and constant sources are not always encountered, which limits the applicability of this approach. It should also be kept in mind that this approach neglects horizontal and vertical dispersion. Thus, it intrinsically assumes that a potential decrease in contaminant concentration due to these processes is due to biodegradation. This can result in an

overestimation of λ. Finally, this approach assumes that biodegradation occurs in the liquid but not in the sorbed phase (ASTM, 1998), as is commonly the case for organic pollutants. If decay occurs also in the sorbed phase (e.g., radioactive materials), the ground water velocity (u) should be replaced by the contaminant velocity (v_c) in eq. (6.9).

Another commonly used method to determine λ involves normalizing BTEX concentrations to those of a recalcitrant compound that was present in the initial release. This reference compound is assumed to behave as a conservative tracer. Trimethylbenzene (TMB) or tetramethylbenzene are commonly used for this purpose. Similar to the Buscheck and Alcantar approach, this technique also requires that the monitoring wells be placed in the centerline of the plume along the main flow direction. Unlike the Buscheck and Alcantar approach, the TMB normalization approach is applicable to non-steady plumes.

Briefly, the TMB normalization approach attempts to discern biodegradation from other processes that decrease contaminant concentrations, such as dispersion, dilution from recharge, and sorption. This is accomplished by normalizing the aqueous concentrations of the BTEX compound of interest to the corresponding TMB concentration (Wiedemeier et al., 1995a):

$$C_{corrected} = C_2 \, (TMB_1/TMB_2) \tag{6.10}$$

Here, $C_{corrected}$ is the normalized concentration of the BTEX compound of interest at (downgradient) point 2, C_2 is the measured BTEX concentration at point 2, TMB_1 is the measured concentration of TMB at point 1, and TMB_2 is the TMB concentration at point 2.

Using Equation 6.10 and assuming first-order biodegradation kinetics, a relationship between first-order rate coefficient (λ) and the corrected contaminant concentrations at two different points can be obtained:

$$C_{corrected, \, d} = C_{corrected, \, u} \, e^{-\lambda t} \tag{6.11}$$

Where $C_{corrected}$ is the TMB-corrected contaminant concentration at the upgradient (u) and downgradient (d) locations, and t is the travel time between the two points.

By rearranging Equation 6.11, λ can be solved for explicitly, which yields a similar expression as Eq. 6.3:

$$\lambda = - \, [\ln(C_{corrected, \, d} / C_{corrected, \, u})]/t \tag{6.12}$$

The travel time (t) between the two points can be determined from the distance (x) traveled by the contaminant divided by the contaminant velocity (v_c):

$$t = x/v_c \tag{6.13}$$

If data are available for more than two wells located along the centerline of the plume, it is recommended to do a linear regression of ln ($C_{corrected}$) vs. travel time to determine the biodegradation rate coefficient. This approach is illustrated in the following example.

<u>Example:</u> The following benzene and trimethylbenzene (TMB) concentrations were measured in a steady plume at three wells placed along the principal flow (x) direction. The groundwater velocity is 0.45 m/day. Assume the retardation factor for benzene is 3.36.

<u>Step 1.</u> Determine the contaminant velocity (v_c) according to eq. (4.1)
$$v_c = 0.45/3.36 = 0.134 \text{ m/day.}$$

<u>Step 2.</u> Determine the travel time (column 2 of Table 8) by dividing the travel distance (column 1 of Table 8) by the contaminant velocity.

Table 8. Benzene and TMB concentrations from well samples along the main flow direction

Distance x (m)	Travel Time t (days)	TMB (µg/L)	Benzene (µg/L)	$(C_{corrected})$* (µg/L)	$\ln (C_{corrected})$
0	0	417	5600	5600	8.63052
6.7	50	400	4260	4441	8.39863
33.5	250	380	3000	3292	8.09925

* $C_{corrected}$ is calculated using equation 6.10, where subscript 1 referring to data for x =0.

<u>Step 3.</u> Perform a linear regression of $\ln(C_{corrected})$ versus t to obtain the slope. The negative of the slope is λ. In this example (Figure 6), $\lambda = 0.0019$ day^{-1}, which corresponds to a half-life of 1.0 year.
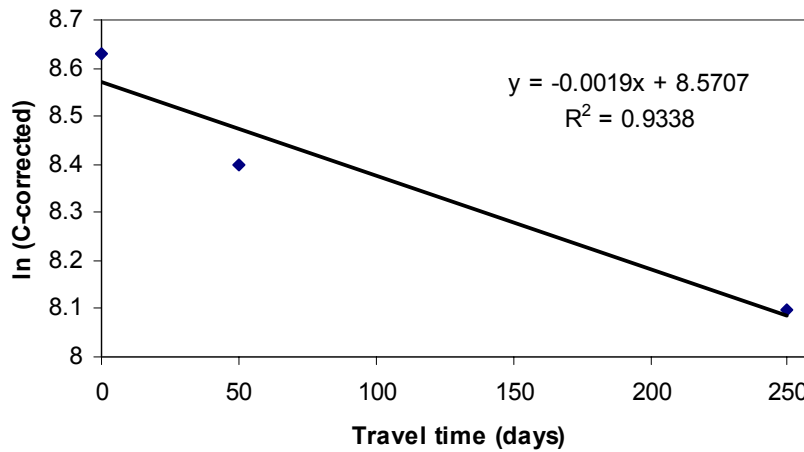

Figure 6. Example of linear regression to determine λ by the TMB normalization method.

It should be kept in mind that TMB is retarded by sorption to a greater extent than BTEX compounds due to its higher hydrophobicity (Table 3). In addition, TMB can be biodegraded to some extent (Wiedemeier et al., 1996). Both of these phenomena increase the BTEX/TMB ratio downgradient form the source, which leads to an underestimation of λ. Since lower λ values are conducive to longer plumes, this approach is considered to be conservative.

In situ microcosms (ISMs) can also be used to determine λ (Gillham et al., 1990a; 1990b; Higgo et al., 1996; Nielsen et al., 1996). ISMs are stainless steel cylinders that isolate about 2 liters of the aquifer, and can be installed using drilling rigs. The device is equipped with valves that

allow for adding the contaminants of interest and for sampling over time from the ground surface. The ISM is open to the ambient aquifer environment at the bottom. Thus, one needs to correct for dilution effects using tracers such as tritium or non-reactive solutes. Since the ISM is hydraulically isolated from the surroundings (aside from capillary exchanges through the bottom) and no replenishment of depleted substrates or electron acceptors will take place during the measurement, the redox conditions should be monitored. Finally, sorption processes may confound the kinetic interpretation of the measurements. Thus, it is suggested that when $K_d < 1$ L/kg, loading of seven pore volumes of spiked groundwater should provide an even distribution of the compound throughout the ISM. This would allow for interpretation of the ISM as a completely mixed batch reactor, and λ to be obtained by fitting the data to equation 6.2. If these conditions are not met, supplementary laboratory sorption studies should be conducted to correct for the disappearance of the added contaminants due to sorption processes.

An alternative method to determine λ is to use well data from the entire site and to use λ as a fitting parameter to a fate and transport model, using non-linear regression techniques. We developed a *bi*odegradation *ra*te *co*efficient *s*oftware (BIRACODES) to perform this task. This software utilizes the three-dimensional analytical solution to the fate and transport equation (Domenico, 1987). The advantages of this software are: (1) it is simple to use and it uses all of the available data for the site (not just data from a few wells along the centerline), (2) it incorporates potential interactions between degradation, advection, and dispersive processes, (3) it does not require the placement of monitoring wells along the flow centerline, (4) it incorporates statistical analyses to determine the 95% confidence interval for biodegradation coefficient and the validity of the model's goodness of fit. However, it is not applicable for unsteady plumes and geological heterogeneities such as interbedded aquifers and aquitards, or zones having hydraulic conductivity contrasts or ranges in organic carbon contents exceeding one order of magnitude along a plume flow path.

DETERMINING IF A PLUME HAS REACHED STEADY STATE

Historical monitoring data collected for the entire plume should be examined to determine if the plume is expanding, steady, or shrinking. This is important for selecting suitable mathematical models to determine biodegradation rate coefficients, and for selecting appropriate remedial actions. If the plume dimensions have not changed significantly over time, and variations in monitoring well concentrations can be attributed to random factors such as water table fluctuations, sampling variability, and analytical uncertainty, the plume can be considered to be at steady state. In essence, this "steady-state" is achieved when any additional contamination released from the source is "naturally attenuated" and degraded at the same rate that it is introduced (ASTM, 1998). As the source is depleted and the main loading rate of constituents of concern to groundwater decreases, the plume begins to shrink.

To determine the status of a plume, monitoring points or other sampling devices should be located to allow the construction of concentration contour maps for BTEX and other constituents of concern. This monitoring map should include a non-detect or compliance level contour (e.g., the drinking water criterion of 5 ppb for benzene) (ASTM, 1998). Based on changes (or lack of changes) over time, the plume can be characterized as shrinking, stable, or expanding.

Alternatively, BTEX concentration(s) in two or more wells located within the plume and downgradient of the source, and oriented along the main flow direction can be monitored over time (ASTM, 1998). The trends in BTEX concentrations will determine if the plume is expanding (i.e., increasing BTEX concentrations), stable (i.e., constant BTEX concentrations), or shrinking (i.e., decreasing BTEX concentrations). One way to visualize such temporal trends is to-plot the measured concentrations for a given BTEX compound at a given well as a function of time (Figure 6). To analyze temporal trends, a linear regression of concentration versus time data would confirm if concentrations are significantly increasing, decreasing, or staying put over time.

The plume should be considered to be at steady state if it meets two conditions. First, it must meet the (Tier-2) steady and declining criteria stipulated in 567 Iowa Administrative code 135.12(6)c. These criteria state that the three most recent consecutive groundwater samples from all monitoring wells must not increase more than 20 percent from the first of the three samples to the third sample; concentrations cannot increase more than 20 percent of the previous sample; and samples must be separated by at least six months. Secondly, as a compatibility constraint for Tier-3 analysis, the slope of the concentration vs. time plot for different wells should not be statistically discernible from zero. This would require performing Student's t-test on the slope of the regression line, with the null hypothesis that the slope equals zero. These statistical tests can be preformed automatically by numerous commercial software packages, including Excel as illustrated below.

Example: The following benzene concentrations were obtained by sampling a well over time

Date	Time (month)	Concentration (ug/L)
1/20/98	0	200
7/21/98	6	210
1/25/99	12	230

Step 1. Test for steady-state. In this case, the concentration increases from the first to third sample. Nevertheless, the concentration from the third sample is only 15% greater than the first sample in the 12-month period. This data set meets the Iowa Tier-2 steady-state criteria.

Step 2. Plot the concentration data vs. time and perform a linear regression. For this example, Excel software was used (Figure 7, Table 9).
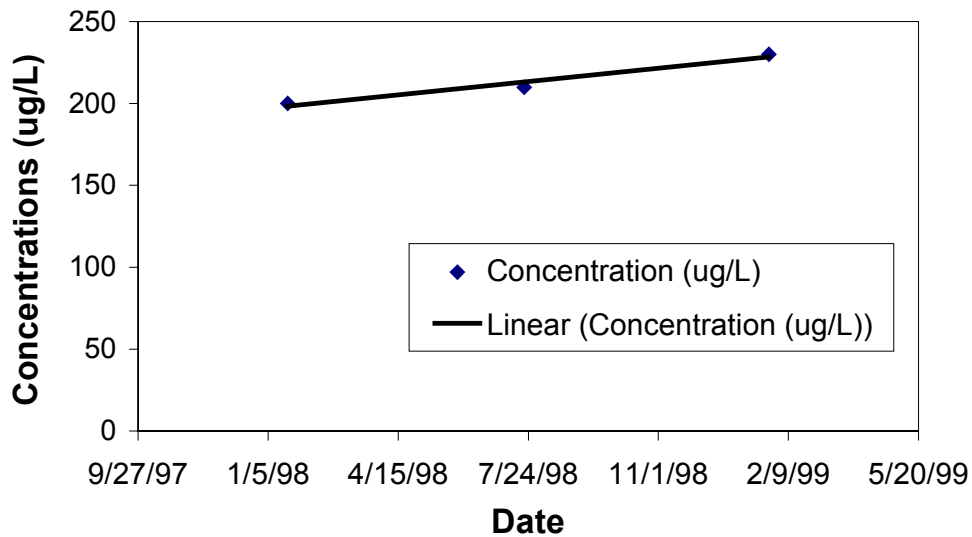

Figure 7. Temporal trends for benzene concentrations downgradient from the source

Table 9. Excel output of regression analysis results for data from Figure 7

Regression Statistics	
Multiple R	0.98198051
R Square	0.96428571
Adjusted R Square	0.92857143
Standard Error	4.0824829
Observations	3

ANOVA

	df	SS	MS	F	Significance F
Regression	1	450	450	27	0.121037718
Residual	1	16.66666667	16.66667		
Total	2	466.6666667			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	198.333333	3.726779962	53.21842	0.011961	150.980307	245.68636
Slope	2.5	0.481125224	5.196152	*0.121038*	-3.613249414	8.6132494

Step 3. Test the data for slope of concentration vs. time equal to zero. Table 9 is the Excel output for the regression analysis. The *p*-value, which represents the attained level of significance for the t-test on the slope, was greater than 0.05 (i.e., *p* = 0.12). Because this slope is not statistically discernible from zero at the 95% significance level, the increase in concentration versus time is not statistically significant. Therefore, this plume meets both criteria to be considered steady.

In general, the steady and declining criteria is more stringent than the Student t test on the slope of the regression line. However, there may be some exceptions to this trend, as illustrated in the following example.

Example: The following benzene concentrations were obtained by sampling a well over time

Date	Time (month)	Concentration (ug/L)
1/20/98	0	100
7/21/98	6	110
1/25/99	12	119

Step 1. Test for steady-state. As shown above, concentrations increase from first to third sample. Since the increase does not exceed the 20% from the first to the last sample, this data set also passes the Iowa Tier-2 steady criteria.

Step 2. Plot the concentration data vs. time and perform a linear regression.

Step 3. Test the data for slope of concentration vs. time equal to zero. In this case, when a regression is carried out (Figure 8), the regression output shows that the increase in benzene concentration over time is statistically significant at the 95% level (i.e., the *p*-value for the slope estimate was 0.019, which is less than 0.05) (Table 10). Therefore, this plume is not steady.
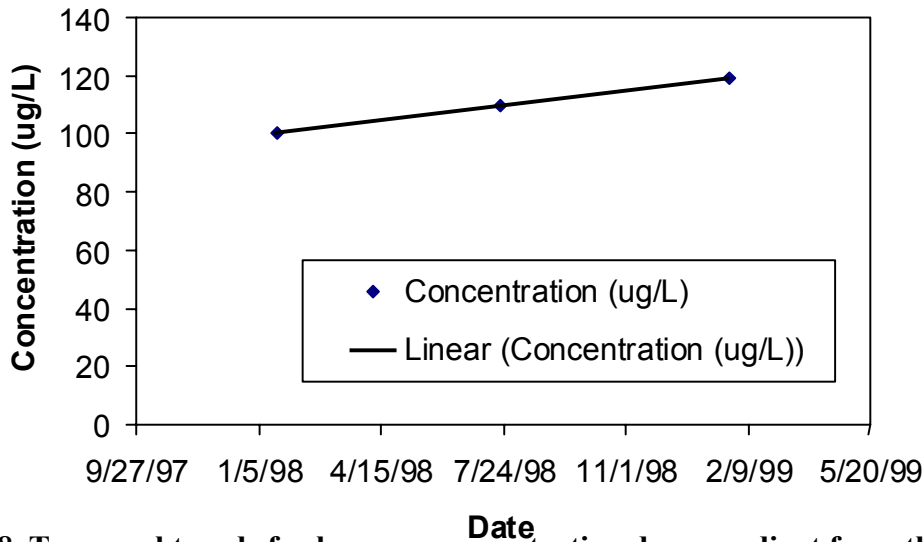

Figure 8. Temporal trends for benzene concentration downgradient from the source

Table 10. Regression analysis results for data from Figure 8

Regression Statistics	
Multiple R	0.99953864
R Square	0.99907749
Adjusted R Square	0.99815498
Standard Error	0.40824829
Observations	3

ANOVA

	df	SS	MS	F	Significance F
Regression	1	180.5	180.5	1083	0.019338923
Residual	1	0.166666667	0.166667		
Total	2	180.6666667			

|	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	100.166667	0.372677996	268.7754	0.002369	95.43136403	104.902
Slope	1.58333333	0.048112522	32.90897	*0.019339*	0.972008392	2.194658

The preceding statistical analyses were carried out using Microsoft Excel Software. Specific instructions to obtain the Excel regression output are provided below.

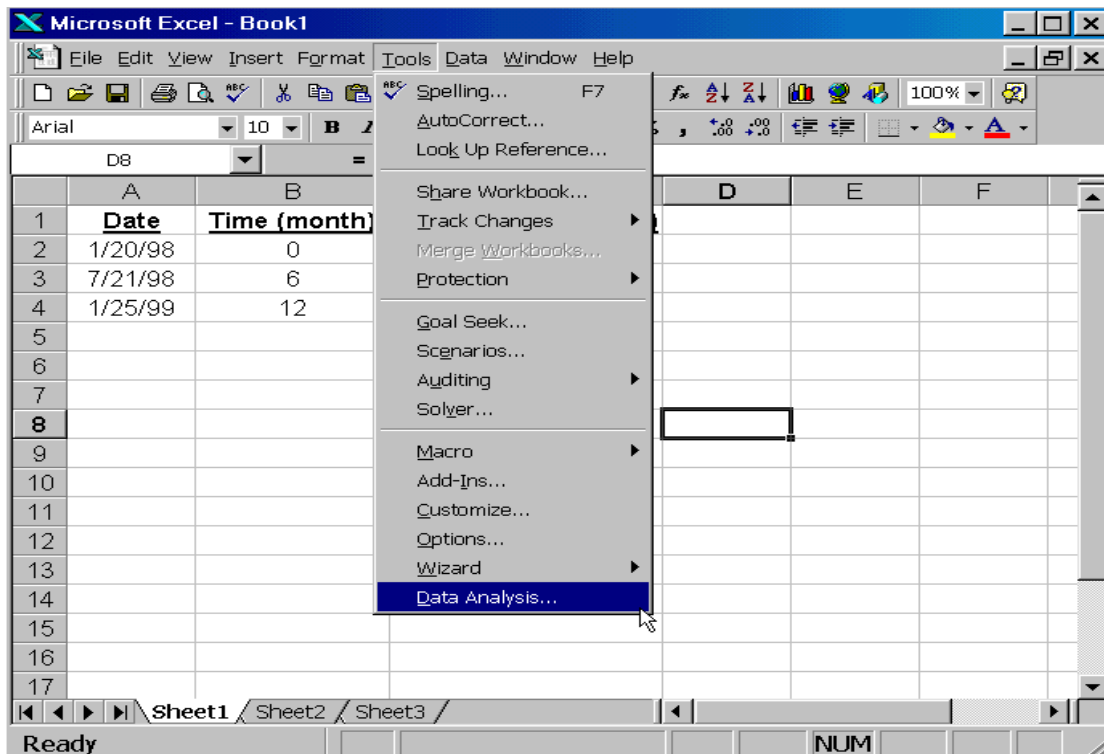1. Open Excel in the window environment
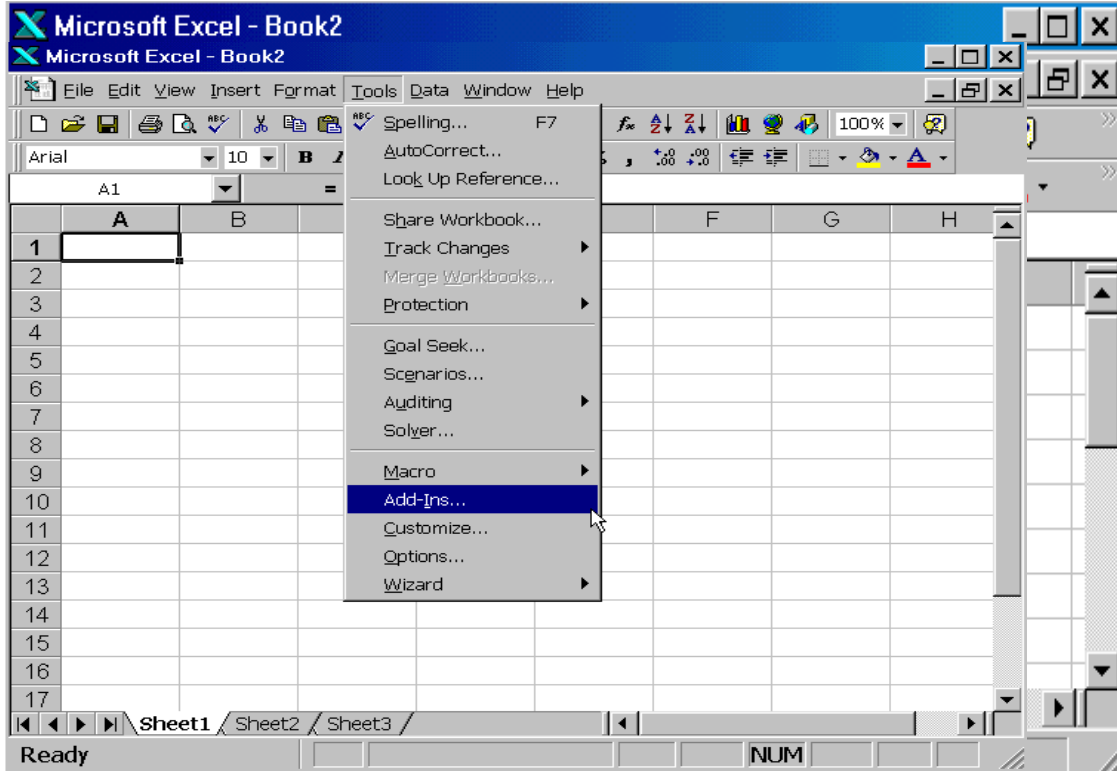
2. Click on "Add-ins" from the "Tools" icon in Excel

3. Check mark "Analysis ToolPak" and "Analysis ToolPak-VBA", then click "OK"
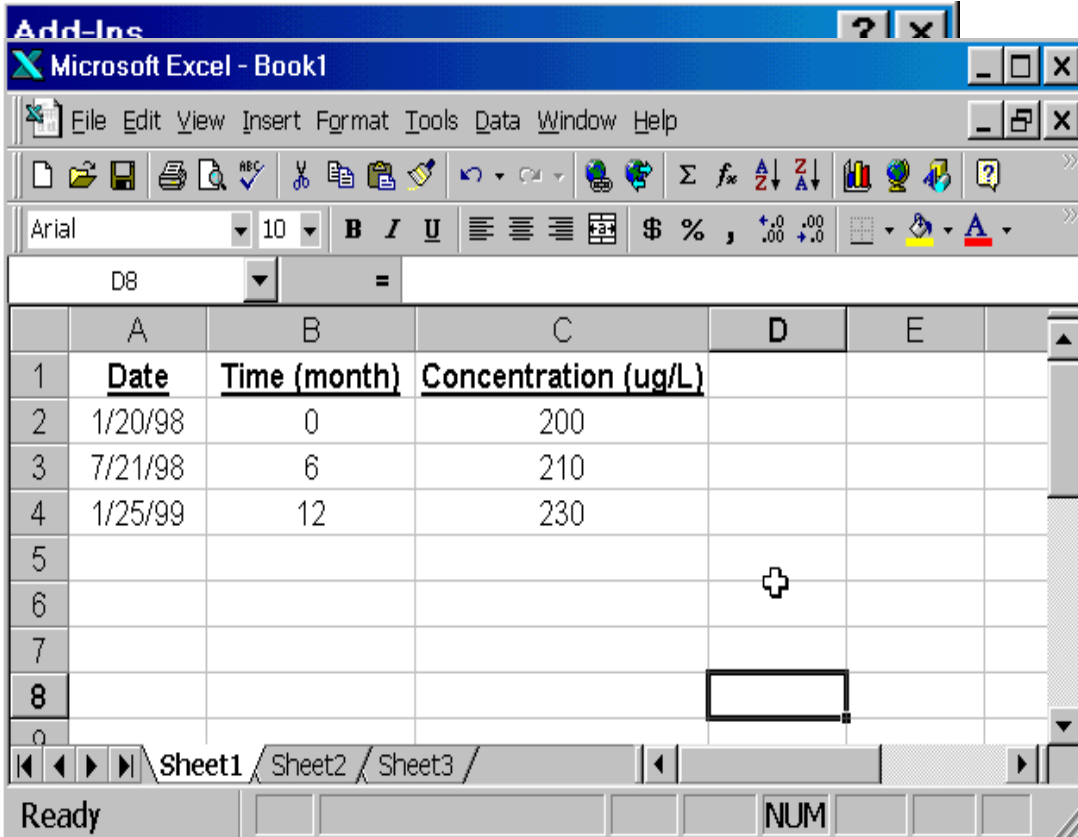
4. In Excel, enter the necessary data for regression (e.g., Table 9)

5. Click on "Data Analysis" from the "Tools" icon in Excel

6. Select "Regression" from the pop-up dialogue box and click "OK"
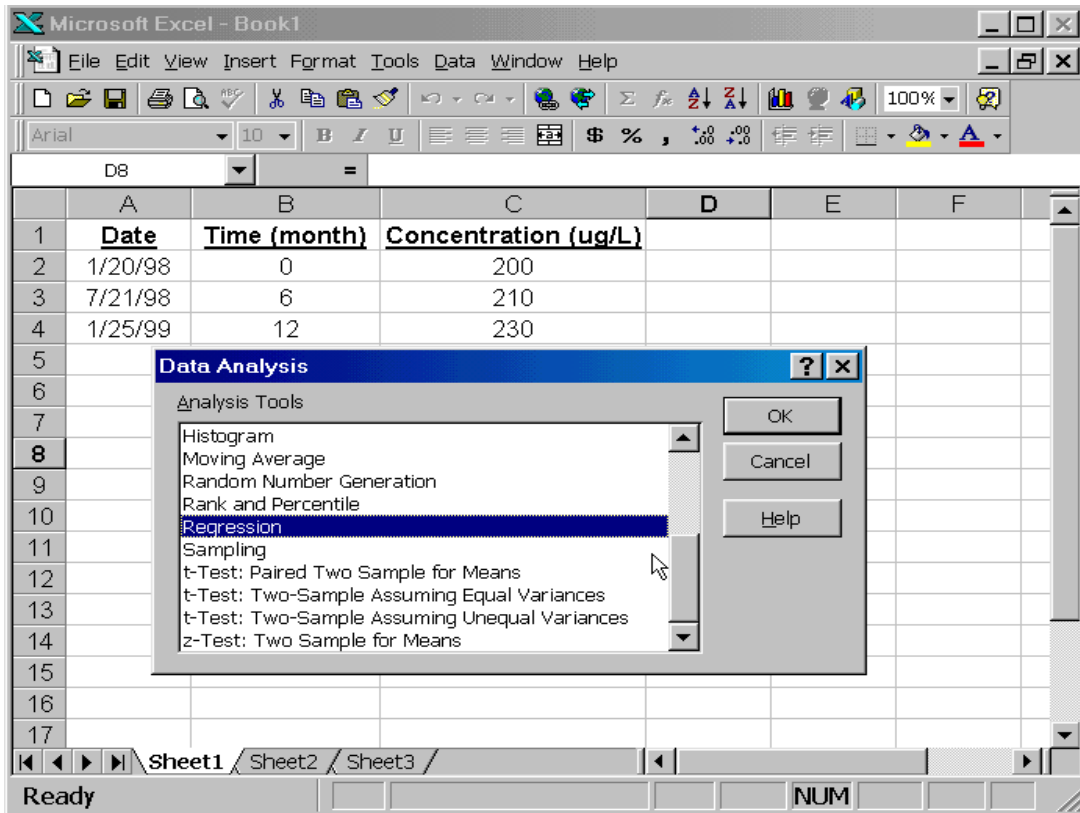
7. Enter the "Y input"-range, which refers to the concentration data. For example, if the concentration data is in column C, rows 2 to 4, then enter C2:C4.
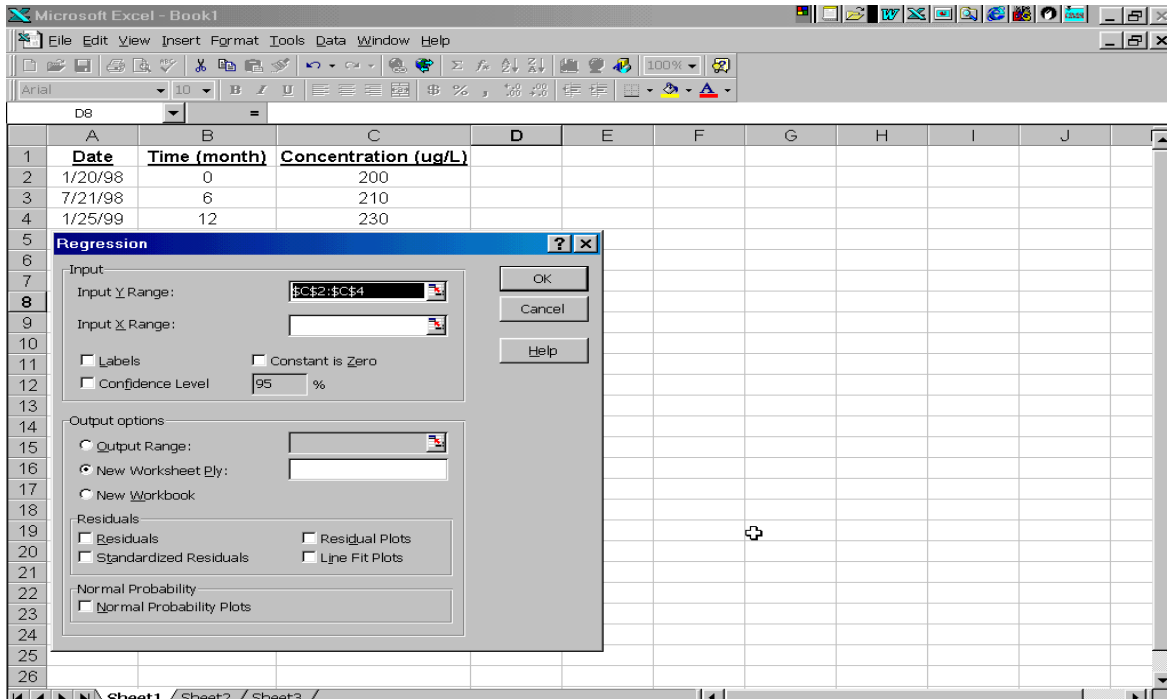
8. Enter the "X input"-range, which refers to the time data. For example, if the time data is in column B, rows 2 to 4, then enter B2:B4.

9. Check mark all of the output needed and click "OK"
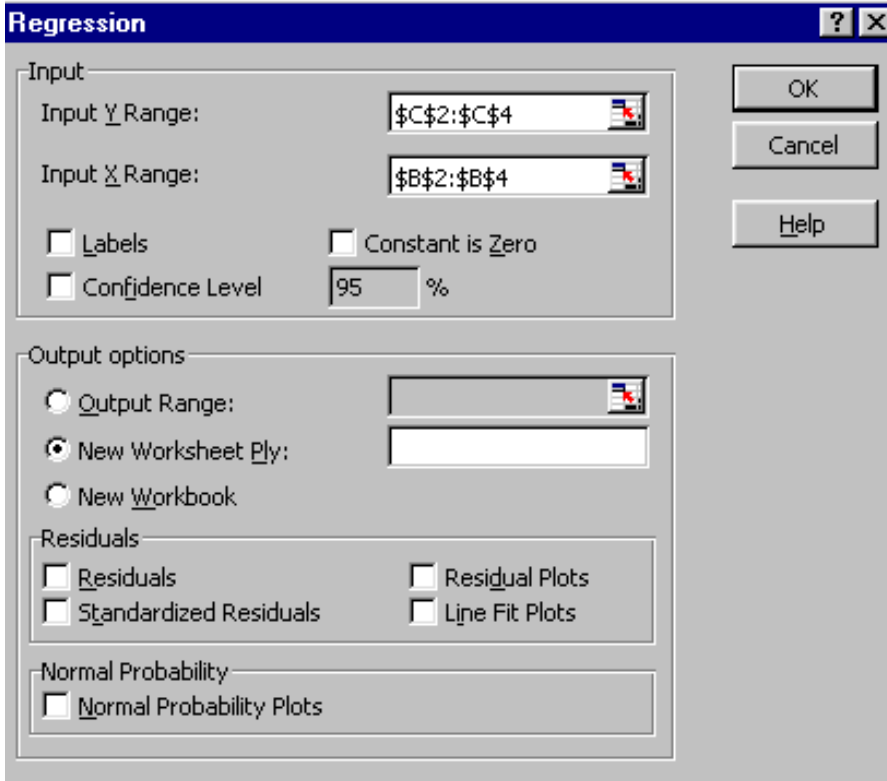
10. A sheet containing the ANOVA (analysis of variance) Table will appear, just like Table10
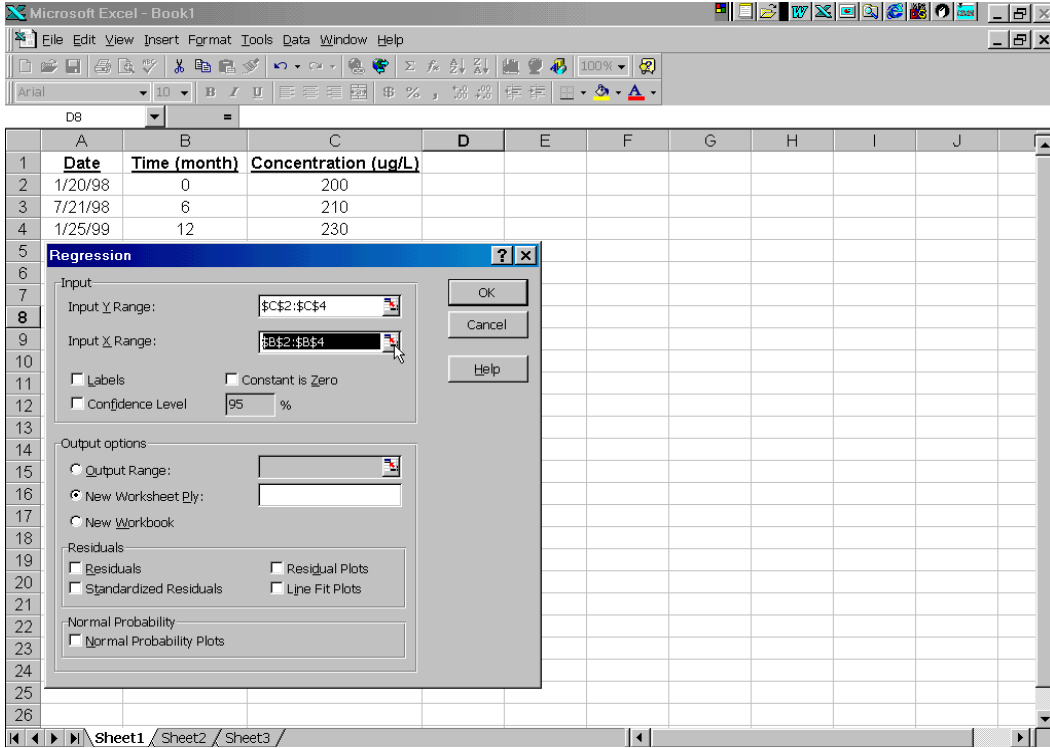
11. For the slope to be statistically undistinguishable from zero (i.e., steady plume) at the 95% confidence level, the *p* value from the ANOVA table has to be greater than 0.05. If *p* < 0.05, the plume is not steady.

It should be kept in mind that the statistical power of the analyses increases with the number of data points available, and that outliers can lead to erroneous conclusions. Therefore, consultation with statisticians on an as-needed basis is recommended.

APPENDIX A
Structure and Properties of Monoaromatic Hydrocarbons

Table A-1. Physical and chemical properties of monoaromatic hydrocarbons

Compound [a]	MW [b] (g/mole)	bp [c] (°C)	mp [d] (°C)	vp [e] (mm Hg)	H [f] (atm.l/mole)	ρ [g] (g/ml)	log K_{oc} [h] (L/kg)	log K_{ow} [i] (L/kg)	Solubility [j] (mg/l)
Benzene	78.11	80.1	5.50	95.19	5.43	0.8737	1.58	2.12	1,791
Ethylbenzene	106.16	136.2	-94.97	4.53	8.44	0.8670	1.98	3.15	161
Toluene	92.13	110.6	-95.0	28.4	5.94	0.8660	2.13	2.73	535
o-Xylene	106.16	144.4	-25.0	6.6	5.1	0.8802	2.38	3.12	175
m-Xylene	106.16	139.3	-47.4	8.3	7.68	0.8684	2.38	3.20	146
p-Xylene	106.16	137.0	13.0	3.15	7.68	0.8611	2.38	3.15	156
Trimetylbenzene	120.19	169..3	-43.8	2.67	5.39	0.8758	--	3.59	64
Tetrametylbenzene	134.22	198	-23.7	0.46	24.9	0.8903	--	--	--

Notes:
[a] See Figure A-1 for chemical structure
[b] Molecular weight (Dean, 1985)
[c] Boiling point (Weast and Lide, 1985)
[d] Melting point (Weast and Lide, 1985)
[e] Vapor pressure (Howard, 1990)
[f] Henry's constant (Howard, 1990)
[g] Density (Weast and Lide, 1985)
[h] log of organic carbon partitioning coefficient (ASTM, 1998)
[i] log of octanol-water partitioning coefficient (Howard, 1990)
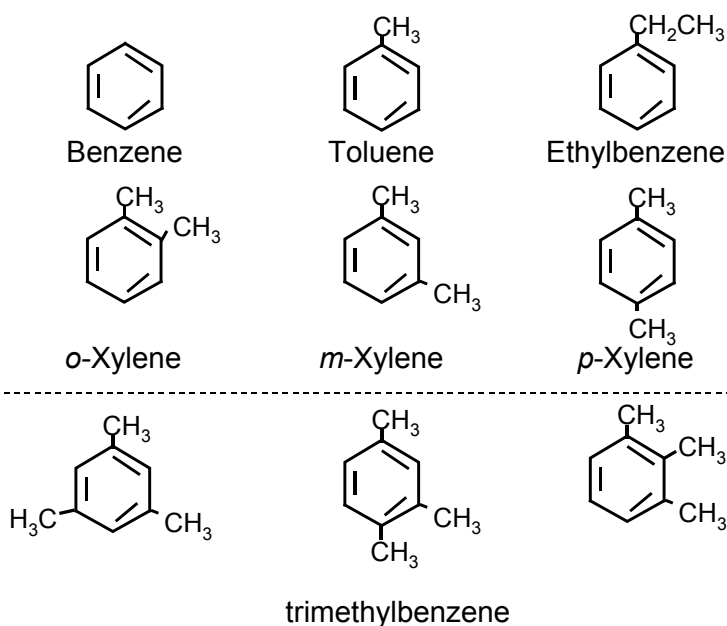[j] Solubility at 25°C (Dean, 1985; Howard, 1990)

Figure A-1. Structure of monoaromatic hydrocarbons

APPENDIX B
Mathematical Expressions for Analytical
Fate and Transport Models

Mathematical expressions for analytical fate and transport models

The mathematical expression from Domenico and Schwartz, 1998 that governs contaminant fate and transport in ground water is given below.

$$\frac{dC}{dt} = D\nabla^2 C - v_c \nabla C - \lambda C \tag{B.1}$$

In this differential equation notation, C is the concentration of a dissolved contaminant at a given point in the aquifer at time t, D is the dispersion coefficient tensor, v_c is the contaminant velocity, λ (lambda) is the first-order decay coefficient, and ∇ is the derivative operator, where $\nabla = \frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z}$ in 3-dimensional Cartesian system. The expression states that the change in contaminant concentration with time is a function of the amount of plume spreading in all directions (first term on the right hand side of Equation B.1, dispersion), the amount of contaminant that migrates with ground water in bulk flow (second term, advection), and the amount of contaminant that is degraded (last term on the right, sink term). The value of the dispersion coefficient is scale-dependent (Zhang and Neuman, 1990), and changes in D that are associated with the scale of experiments or the travel distance of a contaminant are difficult to determine. Therefore, D is usually assumed to be constant in many models, which may introduce an error in model simulations. Groundwater advection under natural conditions, especially at the local scale, usually flows in one direction, which is taken to be x direction here. For the sink term, the decay coefficient (λ) consists of processes such as hydrolysis, photolysis (unlikely if the pollutant is underground), chemical redox reactions, adsorption, volatilization, and biodegradation (Domenico and Schwartz, 1990). However, most studies have shown that the decay coefficient for benzene (and other BTEX compounds) is primarily due to biodegradation (Borden et al., 1994; Chiang et al., 1989; Lovely et al., 1989; Rifai et al., 1995).

Many models are based on solutions to Equation B.1 that incorporate different initial and boundary conditions. These solutions commonly assume the following:

1. The contaminant concentration at time zero is zero (i.e., C(x,y,z,0) = 0).

2. The aquifer is homogenous and isotropic, i.e., K is constant in all directions.

3. The groundwater flow field is uniform, i.e., v_x is constant and $v_y = v_z = 0$.

4. The dispersion is Fickian, the longitudinal dispersivity can be approximated with a constant apparent dispersivity (α_x) and the dispersion coefficient is proportional to the groundwater velocity; i.e., $D_x = \alpha_x v_x$.

5. Adsorption is a reversible process at equilibrium, represented by a linear isotherm.

6. Biodegradation kinetics are first-order with respect to the contaminant concentration.

7. The biodegradation rate coefficient, λ, is constant, which is a very influential assumption.

From the above assumptions, the analytical solution can be obtained for the differential equation (Eq. B.1) and has the form of Equation B.2.

$$C = \left(\frac{C_o}{8}\right) erfc\left[\frac{x - v_c t(1 + 4\lambda\alpha_x/v_c)^{1/2}}{2(\alpha_x v_c t)^{1/2}}\right]\left\{erf\left[\frac{(y + S_w/2)}{2(\alpha_y x)^{1/2}}\right] - erf\left[\frac{(y - S_w/2)}{2(\alpha_y x)^{1/2}}\right]\right\}\left\{erf\left[\frac{(z + S_d)}{2(\alpha_z x)^{1/2}}\right] - erf\left[\frac{(z - S_d)}{2(\alpha_z x)^{1/2}}\right]\right\}$$

$$\exp\left\{\left(\frac{x}{2\alpha_x}\right)\left[1 - \left(1 + \frac{4\lambda\alpha_x}{v_c}\right)^{1/2}\right]\right\} \tag{B.2}$$

This solution to Eq. B.1 is for an infinite domain (i.e., there are no outside boundaries) with a rectangular planar source of dimension (0, S_w, S_d) (Domenico and Schwartz, 1998), shown in the text as Figure 1.

Under the same assumptions and source geometry but with decaying source, the analytical solution to Eq. B.1 is:

$$C = \left(\frac{C_o e^{-kt}}{8}\right) erfc\left[\frac{x - v_c t(1 + 4\lambda\alpha_x/v_c)^{1/2}}{2(\alpha_x v_c t)^{1/2}}\right]\left\{erf\left[\frac{(y + S_w/2)}{2(\alpha_y x)^{1/2}}\right] - erf\left[\frac{(y - S_w/2)}{2(\alpha_y x)^{1/2}}\right]\right\}\left\{erf\left[\frac{(z + S_d)}{2(\alpha_z x)^{1/2}}\right] - erf\left[\frac{(z - S_d)}{2(\alpha_z x)^{1/2}}\right]\right\}$$

$$\exp\left\{\left(\frac{x}{2\alpha_x}\right)\left[1 - \left(1 + \frac{4\lambda\alpha_x}{v_c}\right)^{1/2}\right]\right\} \tag{B.2a}$$

Under the same assumptions and source geometry as above, the steady state solution to Eq. B.1 is:

$$C = \left(\frac{C_o}{4}\right)\left\{erf\left[\frac{(y + S_w/2)}{2(\alpha_y x)^{1/2}}\right] - erf\left[\frac{(y - S_w/2)}{2(\alpha_y x)^{1/2}}\right]\right\}\left\{erf\left[\frac{(z + S_d)}{2(\alpha_z x)^{1/2}}\right] - erf\left[\frac{(z - S_d)}{2(\alpha_z x)^{1/2}}\right]\right\}\exp\left\{\left(\frac{x}{2\alpha_x}\right)\left[1 - \left(1 + \frac{4\lambda\alpha_x}{v_c}\right)^{1/2}\right]\right\} \tag{B.3}$$

<u>Definitions of Variables in Eq. B.2 to Eq. B.3:</u>
C = Contaminant concentration
C_o = Initial contaminant concentration at the source
x = Distance down gradient of source
y = Distance from centerline of source
z = Vertical distance from groundwater surface to the measurement point
S_w = Source width*
S_d = Source depth*
α_x = Longitudinal dispersivity
α_y = Horizontal transverse dispersivity
α_z = Vertical transverse dispersivity
λ = Site-specific first-order decay coefficient
t = Time
k = First-order source decay rate constant
v_c = Contaminant velocity in groundwater
erf = Error function
erfc = Complementary error function = $1 - \text{erf}$

*Note that the Iowa Administration Code (567 IAC Chapter 135.10(2)) defines S_w as the source width of an area where the sum of BTEX concentrations in the groundwater is at a maximum value. Source width measurement should be carried out in the area where groundwater concentrations would be expected to exceed 50 percent of the maximum BTEX value based on linear interpolation. The code stipulates a default value for source depth (S_d) of 3 meters.

APPENDIX C
Example Calculation Employing an Analytical
Model and Site-Specific Parameters

Example calculation employing an analytical model and
Site-specific parameters

One of the purposes of this guideline document is to suggest to ground water professionals how the hydrogeological parameters necessary for confident modeling may be obtained and used in risk assessment at the tier-3 level. This appendix provides an example of
how the Domenico fate and transport models discussed in the text and presented in detail in appendix B can be used in conjunction with high quality, site-specific data to predict the concentration of a chemical of concern at a point of interest down gradient from a contamination source. Predictions of this type are fairly simple with modern spreadsheet software, although setting-up the spreadsheet can be quite tedious and is prone to keystroke errors. The following example is done with Excel. The steady-state model is employed in this example to provide a parallel to the tier-2 formula, which is also steady-state.

Consider a case where tier-2 RBCA modeling based on IDNR default values and very limited site data has shown that the benzene plume will affect a drinking water receptor at a distance of 120 meters down gradient from a gasoline release source. Closure of the receptor is not an option, and active remediation will be prohibitively costly. A tier-3 assessment is thus a speculative, but attractive option. A lengthy site monitoring record permits confident estimation of λ, and indicates the plume is not growing. Additional site characterization proceedes to develop reliable estimates for K, f_{oc}, ρ_b, and n for the soil, that is developed on weathered, clayey till.

An Excel spreadsheet is constructed listing all of the site parameters in an orderly data
table, with formulae to calculate the advective velocity (Equation 2.3) and retarded velocity (Equation 4.1) entered as shown in Figure C.1.

Formulae for the error function and exponential terms in the Domenico steady-state model (Equation B.3) are set in cells I10 – I14 of figure C.1, and these results are combined in cell H18 in a formula to calculate C/C_o. The Excel formulas for these terms are given below. Be aware that the erf (and erfc) functions in Excel must have positive values for the terms in parentheses, so for the situation where S_w or S_d are greater than "y" or "z", respectively, the formula must be modified by using the error function identity:

$$\text{erf}(-\beta) = -\text{erf}(\beta)$$

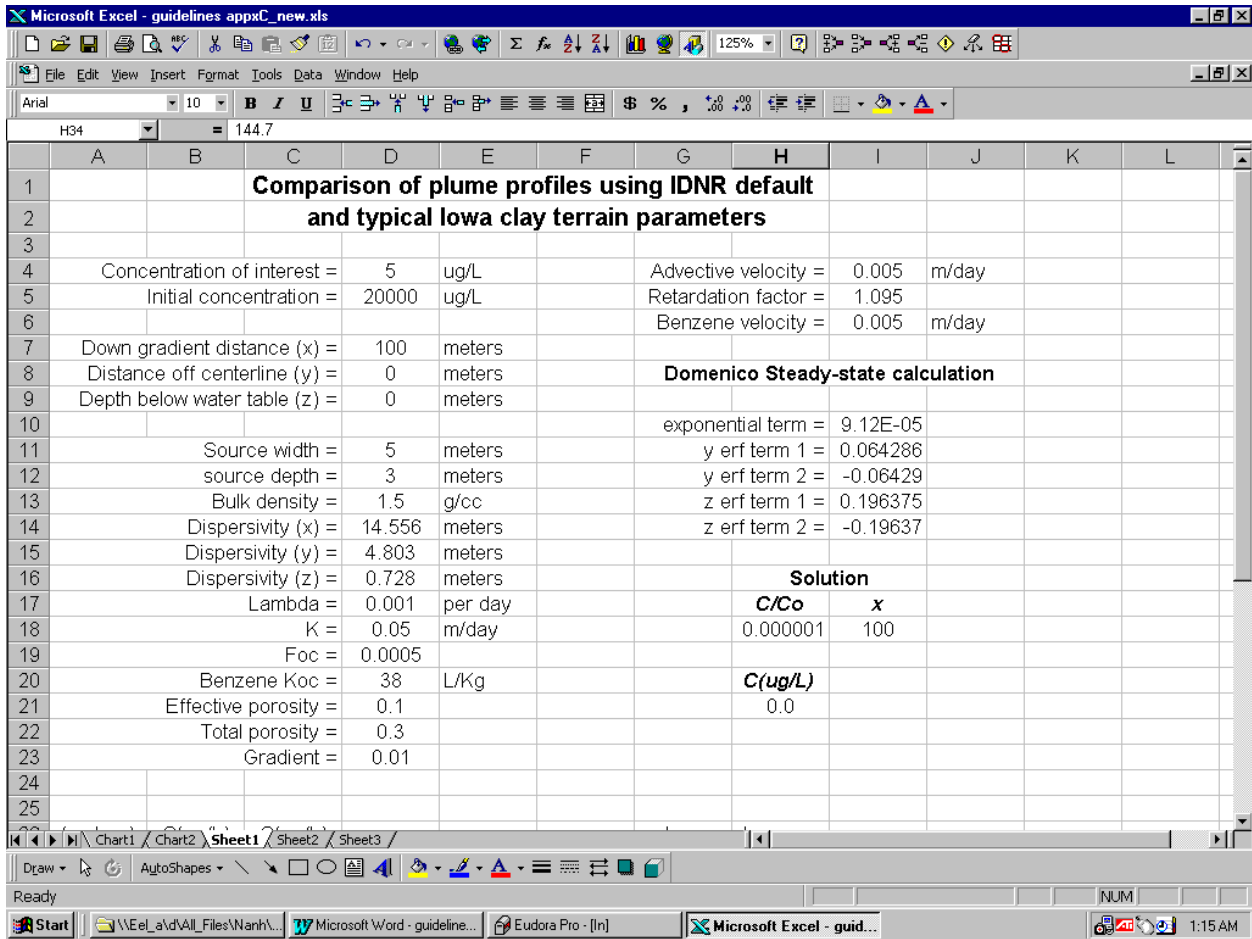|	
First y-term (I11)	= ERF((D8+D11/2)/2/SQRT(D15*D7))
Second y-term (I12)	= -ERF(-(D8-D11/2)/2/SQRT(D15*D7))
First z-term (I13)	= ERF((D9+D12)/2/SQRT(D16*D7))
Second z-term (I14)	= -ERF(-(D9-D12)/2/SQRT(D16*D7))
Exponential term (I10)	= EXP((D7/2/D14)*(1-SQRT(1+4*D17*D14/I6)))

Figure C.1: A sample of spreadsheet set-up in calculating plume dimensions.

The solution (C/C_o), found in cell H18, is the steady-state concentration along the plume center line (y = 0), at the water table (z = 0), at the down gradient distance of interest (x). The following formula is entered in that cell and combines the above terms according to equation B.3:

$$=0.25*I10*(I11-I12)*(I13-I14)$$

With knowledge of the source concentration at this site, for example C_o = 20,000 ug/L, the steady-state benzene plume can be modeled for down gradient distances of interest simply by plugging successive values for x into the data table, and converting the result in cell H18 from C/C_o to C(ug/L). This algorithm was done utilizing first the IDNR default parameters, then again utilizing specific parameters one might find at a site on clayey soil (Table C.1).

The resulting plume profiles are compared in Figure C.2. Based on this relatively inexpensive tier-3 effort, which was produced utilizing site-specific data of high reliability, an expensive, active remediation system is shown to be unnecessary. According to Figure C.2, the 5 ug/L contour in the benzene plume is expected to extend no further than 45 meters when it reaches steady state.

For completeness, additional scenarios can be modeled to bracket the upper and lower limits of any parameters, thereby demonstrating a range of likely plume lengths for reasonable variations in K, f_{oc}, etc. If the modeled solution found in this example is thus adequately justified, it appears that source removal and monitoring at a sentinel well should protect the drinking water well. It should be kept in mind, though, that a different result will be obtained if the benzene source is not constant, but that solution is left to the reader.
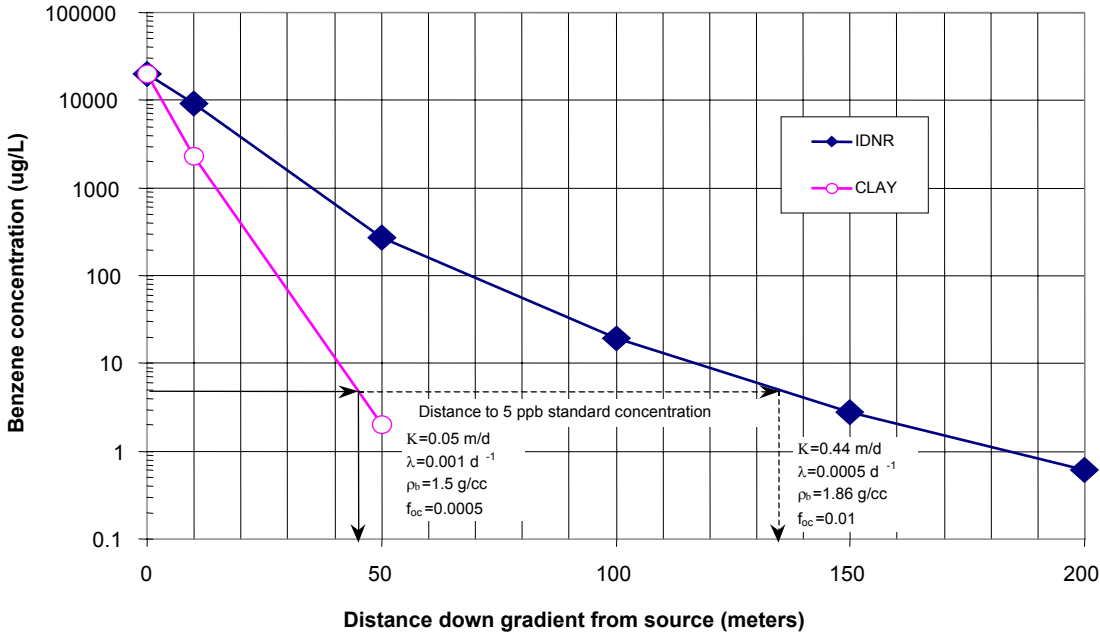
Figure C.2: Comparison of steady-state plume profiles using Equation B.3 with IDNR default and typical clay site parameters. Dispersion term calculated with equation 5.5a.

Table C-1: Parameter values used in simulating plumes from various sources

Parameter	IDNR default	Site-specific
Distance from centerline (m)	0	0
Depth below water table (m)	0	0
Source width (m)	5	5
Source depth (m)	3	3
α_x (m)	10	$0.0175(L^{1.46})$
α_y (m)	3.3	$0.33\alpha_x$
α_z (m)	0.5	$0.05\alpha_x$
λ (day^{-1})	0.0005	0.001
ρ_b (g/cm^3)	1.86	1.50
Effective porosity (θ_e)	0.1	0.1
K (m/day)	0.44	0.05
f_{oc}	0.01	0.0005
Gradient	0.01	0.01
K_{oc} (L/Kg)(benzene)	38	38

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