

# A Comparison of Zero-Order, First-Order, and Monod Biotransformation Models

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# A Comparison of Zero-Order, First-Order, and Monod Biotransformation Models

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## Abstract

Under some conditions, a first-order kinetic model is a poor representation of biodegradation in contaminated aquifers. Although it is well known that the assumption of first-order kinetics is valid only when substrate concentration,  $S$ , is much less than the half-saturation constant,  $K_S$ , this assumption is often made without verification of this condition. We present a formal error analysis showing that the relative error in the first-order approximation is  $S/K_S$  and in the zero-order approximation is  $K_S/S$ . We then examine the problems that arise when the first-order approximation is used outside the range for which it is valid. A series of numerical simulations comparing results of first- and zero-order rate approximations to Monod kinetics for a real data set illustrates that if concentrations observed in the field are higher than  $K_S$ , it may be better to model degradation using a zero-order rate expression. Compared with Monod kinetics, extrapolation of a first-order rate to lower concentrations under-predicts the biotransformation potential, while extrapolation to higher concentrations may grossly over-predict the transformation rate. A summary of solubilities and Monod parameters for aerobic benzene, toluene, and xylene (BTX) degradation shows that the *a priori* assumption of first-order degradation kinetics at sites contaminated with these compounds is not valid. In particular, out of six published values of  $K_S$  for toluene, only one is greater than 2 mg/L, indicating that when toluene is present in concentrations greater than about a part per million, the assumption of first-order kinetics may be invalid. Finally, we apply an existing analytical solution for steady-state one-dimensional advective transport with Monod degradation kinetics to a field data set.

## Introduction

As problems with using pump and treat systems to clean contaminated ground water have become more apparent, *in situ* bioremediation has been gaining momentum as a viable alternative. Two strategies of *in situ* bioremediation exist: enhanced remediation where the process is stimulated by adding nutrients or electron acceptors; and intrinsic remediation or natural attenuation where the natural process is documented and monitored. The case for remediation by natural attenuation of petroleum hydrocarbons has been strengthened by a recent study of groundwater plumes from leaking underground fuel tanks (LUFTs) in California (Rice et al. 1995a). The study results suggest that LUFT plumes rarely exceed 250 m in length and either stabilize or shrink over time. Based on these results, Rice et al (1995b) recommended that the state allow natural attenuation as a treatment option for LUFT plumes.

A necessary step in the evaluation of the bioremediation potential of a field site is the construction of a model describing the transport and biodegradation of the compounds in a contaminant plume. Several mathematical expressions are available for describing the rate of biotransformation. The most prominent are the Monod or Michaelis-Menten expression, and its first- and zero-order approximations. Of these, the first-order approximation, with the rate constant expressed as a percent loss of the target compound(s) per day, is the most frequently used (see Salinitro (1993)). Although first-order rates are convenient, their suitability for describing biodegradation rates depends on the assumption that the maximum concentration of the rate-limiting species is much less than the value of the half-saturation constant. It is not possible to know the value of the half-saturation constant for a system without fitting a Monod kinetics model to either field or microcosm degradation data. Comparing existing measurements of the half-saturation constant for BTX compounds with maximum observed concentrations at contaminated sites suggests that the first-order model is probably widely misapplied. Although this problem has been noted before (see Alexander and Scow, 1989), its consequences have not been examined in detail. The misuse of first-order kinetics obscures the relative effects of a number of different factors that influence rates of natural attenuation. These effects include dispersion, contaminant concentrations, electron acceptor concentrations, nutrient availability (Allen-King et al., 1994b), the microbial populations (Godsy et al., 1992; Allen-King et al., 1994a), interference between multiple compounds (Chang et al., 1993), diffusion and desorption limitations (Scow and Hutson, 1992), and dissolution rates of non-aqueous phase sources. The most important problem, however, is that the use of a single first-order rate to represent the observed degradation process when the correct model is Monod kinetics, can lead to significant errors in prediction. In particular, an accurate estimate of the expected natural attenuation clean-up time for a plume depends on knowing the correct degradation kinetics.

Frequently the justification for the use of first-order approximations is that they correctly describe the observed transformation rate in the field. This assertion should be carefully examined because the data are often analyzed by performing a linear fit on a semi-log plot. Because the variability of the data is less apparent in semi-log space than in linear space, a fit of this type may look deceptively good. A further justification is that the site clean-up may proceed as predicted by the simpler model. In some cases this will be because all of the necessary conditions needed to justify the use of first-order rates are met. In general, however, neglecting to verify that the assumptions are valid can lead to rate estimates that are grossly wrong and result in inaccurate model projections for risk-based analyses of a site. A less dramatic but perhaps more important problem, in the long run, is that our understanding of the basic processes controlling the biodegradation rate is obscured by the wide-spread use of first-order rates.

On the basis of a linear appearance of the data in linear space, several authors have found that a zero-order model best fits lab and field data (e.g., Barker et al., 1987, Nielsen and Christensen, 1994, Allen-King et al., 1994a, Reinhard et al., 1997). However, zero-order models are problematic for prediction because they result in negative concentrations. Starr and Parlange (1976) showed that a fit of concentration data without knowing the biomass distribution is inadequate to distinguish between a first- and zero-order model. The validity of the Monod model over a broad range of substrate concentrations and conditions has been demonstrated repeatedly since its publication (Monod, 1949; Grady and Lim, 1980). The use of a simpler model may be

convenient but it should be considered purely descriptive and should not be used to predict transformation rates outside the range of concentrations for which data exist.

The purpose of this paper is to analyze the accuracy of first- and zero-order approximations for Monod kinetics. We first present a review of Monod kinetics and derive the first- and zero-order approximations and their associated errors. Next, we use the full Monod expression and the two approximations to model a real data set and analyze where each succeeds or fails. To evaluate the appropriateness of approximations, we review published values of Monod degradation parameters for aerobic BTX degradation and compare them with concentration ranges found in the field. Finally, we apply a simple analytical solution (Parlange et al., 1984) to the steady-state one-dimensional advective equation that incorporates full Monod kinetics. This solution may be used to determine the values of Monod parameters from field or microcosm data.

### Theoretical Approximation Error

Monod (1949) presented the differential equations that describe the utilization of a single rate limiting substrate and resulting microbial growth by a pure culture of microorganisms suspended in liquid at a constant temperature:

$$\frac{dS}{dt} = -\frac{\mathbf{m}_m}{Y} B \left[ \frac{S}{K_S + S} \right]; \quad (1a)$$

$$\frac{dB}{dt} = \mathbf{m}_m B \left[ \frac{S}{K_S + S} \right], \quad (1b)$$

where  $S$  is the substrate concentration (mg/L);  $t$  is time (day),  $\mathbf{m}_m$  is the maximum specific growth rate ( $\text{day}^{-1}$ );  $Y$  is the biomass yield (mg biomass/mg substrate);  $B$  is the biomass concentration (mg biomass/L); and  $K_S$  is the half-saturation constant (mg/L). In the Monod formulation, the rate of the transformation increases with the substrate concentration,  $S$ , but as  $S$  grows large, the rate asymptotically approaches a maximum value given by  $(\mathbf{m}_m/Y)B$ . Thus, the fastest possible transformation rate depends on both the biomass concentration and the maximum utilization rate per unit biomass. The asymptotic approach to the maximum rate is controlled by the relative values of  $S$  and  $K_S$ . The half-saturation constant,  $K_S$ , is the concentration of substrate at which the transformation rate is half the maximum value. For the purpose of this analysis, we assume that the biomass stays constant in time. This assumption is justified by the relatively small change in the number of active degrading microbes found in aquifer sediments that have been exposed to contaminants for several years (e.g. Godsy et al., 1992; Allen-King et al., 1994b). We may then drop equation (1b) and group three constants in equation (1a) into one new constant called the substrate utilization rate,  $v_m = \mathbf{m}_m B/Y$  (mg /L-day). The simplified equation is the same as that given by Simpkins and Alexander (1984) for the case of Monod, no-growth:

$$\frac{dS}{dt} = -v_m \frac{S}{K_S + S} . \quad (2)$$

Two linear approximations for equation (2) have been formulated (see e.g. Horan, 1990). The choice of approximation to use for a particular application depends on the relative values of  $S$  and  $K_S$ . When  $S$  is several times smaller than  $K_S$  ( $S \ll K_S$ ), equation (2) may be approximated by a first-order equation:

$$\frac{dS}{dt} = -\frac{v_m}{K_S} S . \quad (3)$$

Frequently the Monod parameters in (3) are combined to give  $k = v_m/K_S$  ( $\text{day}^{-1}$ ) where  $k$  is known as the first-order rate constant. The value of  $k$  is obtained by finding the slope of the best fit line on a plot of the natural log of concentration versus time. When  $S$  is several times greater than  $K_S$  ( $S \gg K_S$ ) then (2) may be approximated by a zero-order equation:

$$\frac{dS}{dt} = -v_m . \quad (4)$$

The value of the zero-order rate constant  $v_m$  is obtained by finding the slope of the best fit line on a plot of concentration versus time in linear space.

We derived absolute and relative errors in the degradation rates associated with each of the approximations (3) and (4) as follows. The Monod expression in (2) was split into two parts such that the first term is one of the approximations and the second term is the associated absolute error. For the first- and zero-order expressions, respectively, this yields:

$$\frac{dS}{dt} = -\frac{v_m}{K_S} S + \frac{S}{K_S} \left[ \frac{v_m S}{K_S + S} \right] , \quad (5)$$

$$\frac{dS}{dt} = -v_m + \frac{K_S v_m}{K_S + S} . \quad (6)$$

Each error can be expressed as a relative percentage by subtracting the approximation from the full expression (5) or (6); dividing by the full Monod expression in (2); and taking the absolute value, to give:

$$e_1 = \frac{S}{K_S} \times 100\% ; \quad (7)$$

$$e_0 = \frac{K_S}{S} \times 100\% ; \quad (8)$$

for the first- and zero-order approximations, respectively. The result in (7) shows that for the first-order approximation, the error will be small when  $S$  is much less than  $K_S$ . For example, the error will be less than 10% when  $S < 0.1K_S$ . However, as  $S$  increases, the error quickly becomes quite large. Thus, if  $S = 10K_S$ , the error will be an impressive 1,000%. The zero-order case is opposite. In particular, the error is less than 10% whenever  $S > 10K_S$  and greater than 1,000%

when  $S < 0.1K_S$ . Clearly, the relative values of  $S$  and  $K_S$  have a significant effect on the approximation error.

In both (5) and (6) the error terms are positive, indicating that, when the true Monod parameters are used in the approximate expressions, the results always predict a higher degradation rate than the full kinetic expression in (2). This over-prediction violates a common engineering design criterion that any bias introduced by an approximation should be toward a more conservative estimate. Typically, however, the Monod parameters are not known so either (3) or (4) is fit directly to the data to obtain a first- or zero-order decay constant. In this case the above error analysis does not strictly apply. However, the above analysis suggests that the use of one of the approximate models outside its valid range is problematic. Thus, if a first-order rate is obtained from a data set without examining the relation of  $S$  to  $K_S$ , the use of this rate for prediction or extrapolation should be highly suspect. To illustrate the nature of the problems that may arise, we compared the results of fitting Monod, zero-order, and first-order models to a laboratory data set.

### Graphical Evaluation of the Approximations

Figure 1 shows the phenol and biomass concentrations obtained during methanogenic degradation of phenol in a batch laboratory microcosm. The batch microcosms were prepared according to the methods in Godsy et al. (1992). Sufficient nutrients were available to ensure that phenol was the rate-limiting substrate. Because of the low biomass yields of the methanogenic consortia, the growth of the biomass on the phenol is minor. Therefore, we can simplify our analysis by assuming that the biomass remains constant, and that the transformation rate can be approximated by equation (2). Using nonlinear regression we obtain the values,  $v_m = 1.39$  mg/L-day and  $K_S = 1.7$  mg/L to describe the Monod no-growth kinetics of the phenol transformation. We will now

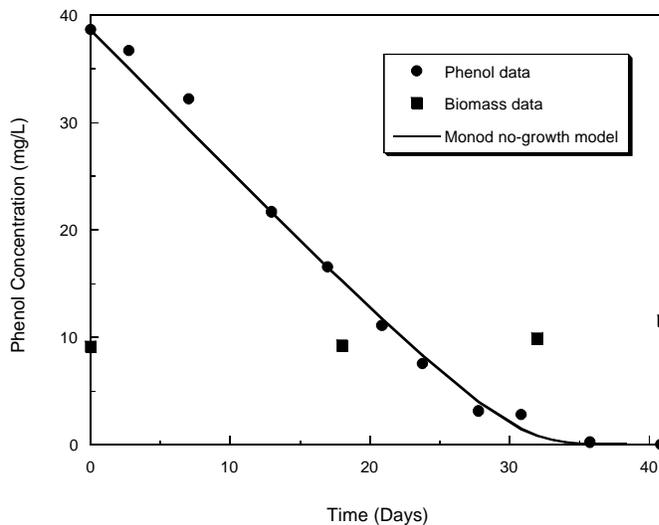


Figure 1: Phenol and biomass concentration data from methanogenic degradation of phenol in a batch laboratory microcosm together with a fit of the no-growth Monod kinetics equation (2).

assume that the profile described by these parameters represents the “true” degradation model and use it to evaluate the validity of three possible approximations: two first-order models with rates based on different concentration ranges and one zero-order model with a rate based on all but the last data point.

To obtain estimates for the rate constant in the first-order approximation (3) the phenol data are plotted in Figure 2a with the natural log of concentration versus time. If a first-order rate applies, the data points should fall along a line. Instead, they form a concave-down profile, precluding a reasonable linear fit over the full range. In general, a concave

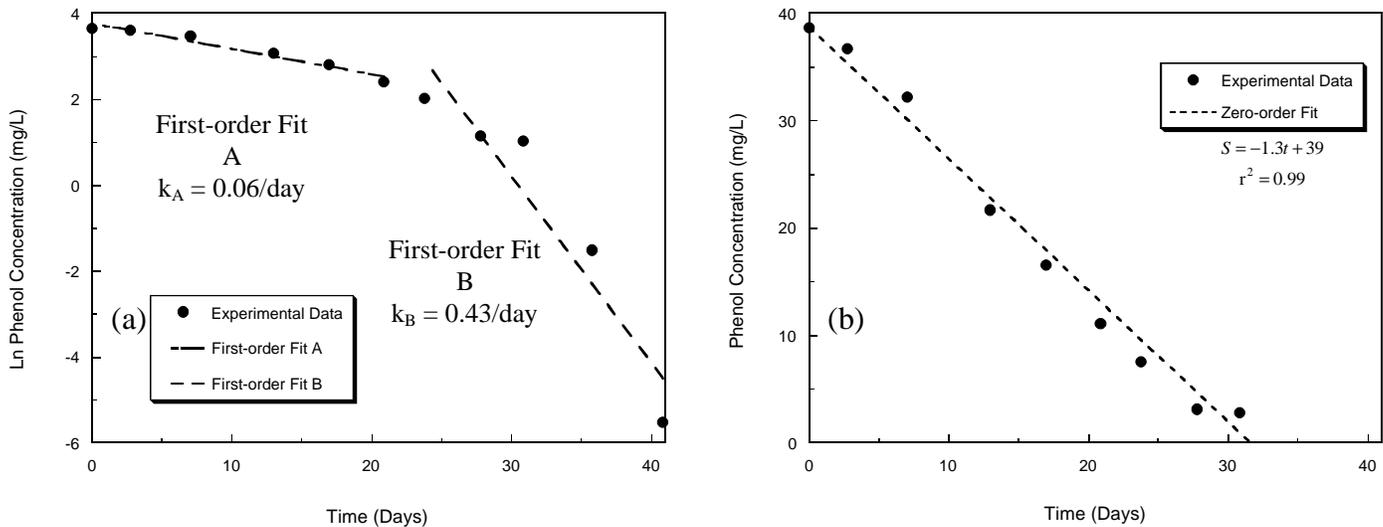


Figure 2: (a) Laboratory phenol degradation data with natural log of concentration versus time. Two lines denoted A and B were fit by linear regression to the high (10-40 mg/L) and low (under 10 mg/L) concentration portions of the data. (b) A linear regression of a zero-order kinetics rate to the phenol data using all but the last two points in the phenol data set. R-squared values for each fit are shown together with the best-fit parameters.

down profile of log concentration versus time is evidence that a Monod model applies. One might be tempted to conclude that two first-order rates are present. However, in this case, the initial concentration is much greater than the half-saturation constant so a first-order model is not valid. We will now attempt to fit these data with two first-order rates to illustrate the problems with using the wrong model formulation. The two fitted first-order rates are shown in Figure 2a together with their r-squared values. Neither of the fits are reasonable for the full data set, but it is not difficult to imagine that partial data sets could be obtained and analyzed to produce similar values. Note that the two rates roughly differ by an order of magnitude. Salinitro (1993) states that first-order rates measured in lab microcosms are frequently an order of magnitude higher than field rates. Regardless of other influences, this result may be obtained solely by fitting first-order models to lab and field data with different starting concentrations.

Fit A (Figure 2a) might be typical of scenarios where only the observed field concentrations are analyzed. Here, the final concentration used in the fit is 11.1 mg/L, or  $6.5K_S$ . Because biodegradation in the field is often oxygen-limited, the concentrations for some compounds may initially decrease and then level off as the background oxygen supply is exhausted. This would result in evidence of degradation spanning the higher concentrations but no degradation in the range less than or equal to  $K_S$ . In the case of fit B (Figure 2a), the highest concentration used in the regression is 7.6 mg/L, or about  $4.5K_S$ . This might be considered a reasonable initial value for a laboratory microcosm study. A review by Salinitro (1993) of BTX compounds lists several laboratory rate studies with lower starting concentrations. Even if a higher initial concentration was used, one possible reason for choosing to fit the lower concentration range is a subjective impression that the slope of the concentration curve is low for values above 10 mg/L. In this case, the use of the semi-log plot is deceptive because 75% of the mass loss by biotransformation occurs in the initial apparent low-slope region of the curve. (See Baedecker (1994) for a discussion of field data with this profile). One might be tempted to assume that losses in this

region were due to volatilization and that the biodegradation rate was represented by the steeper part of the curve. However, on the basis of our killed control data, we have verified that losses due to volatilization of phenol are insignificant in this experiment.

Figure 2b shows the fitted zero-order expression for the data set. The fit was obtained using all but the last two points in the phenol data set because these values are well below the range where a zero-order approximation is valid. Note that the r-squared value is higher than for either of the first-order fits. The zero-order fit is particularly successful here because most of the phenol concentrations are higher than the half-saturation constant,  $K_S = 1.7$  mg/L.

To illustrate the importance of the relation between the initial concentration and the value of  $K_S$ , we compare the three approximations to the Monod predictions for initial concentrations of phenol of 39, 3.9, and 0.39 mg/L. The results are plotted in Figures 3-5. In each plot, the curve labeled Monod represents the “true” degradation profile simulated with equation (2) using the fitted Monod parameters from Figure 1. The two first-order curves were generated with equation (3) using the rates from the A and B fits (Figure 2a). Finally, the zero-order simulation was generated with equation (4) using the fitted rate from Figure 2b. The data points shown are the phenol concentrations from Figure 1 but shifted in time as though the experiment started at the given initial concentration. As a consequence, there are only two data points for comparison in Figure 5. The important point, however, is that different initial concentrations can affect judgments about which model applies and the values of the parameters obtained.

Figure 3 shows the experimental data together with the four possible models on a linear scale. From the plot, it is clear that the zero-order rate is the better approximation for concentrations above 3.0 mg/L which is consistent with our error analysis. The first-order fit B predicts transformation rates that are much too rapid. This illustrates the pitfalls associated with taking a first-order rate determined from low starting concentrations and using it to predict the fate for

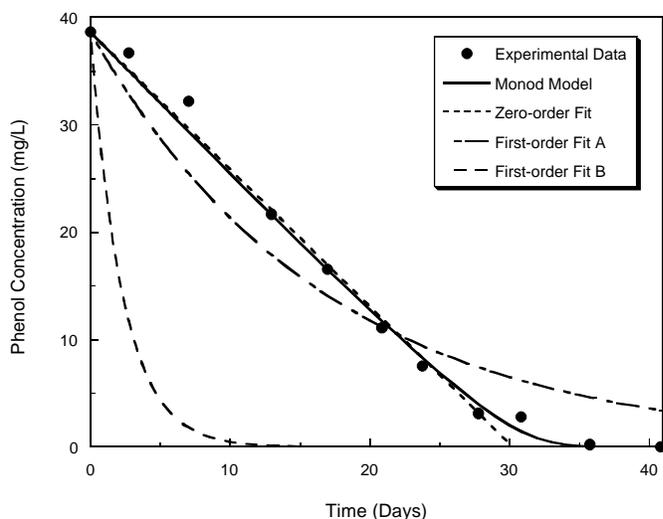


Figure 3: Phenol data together with results from four models: Monod; first-order fit A; first-order fit B; and the zero-order fit for a starting concentration of 38.7 mg/L.

higher starting concentrations. The opposite problem is encountered with the first-order fit A. In this case, the predicted substrate concentrations are reasonable above 10.0 mg/L but are too high below this value. This is typical of the errors involved in using a first-order fit from high concentrations to predict the rate for low concentrations. The fact that the error in first-order curve is conservative may seem to justify its use. However, we shall show below that for lower starting concentrations, the fit from A is excessively conservative.

Figure 4 compares the first- and zero-order approximations to the Monod curve for an initial substrate

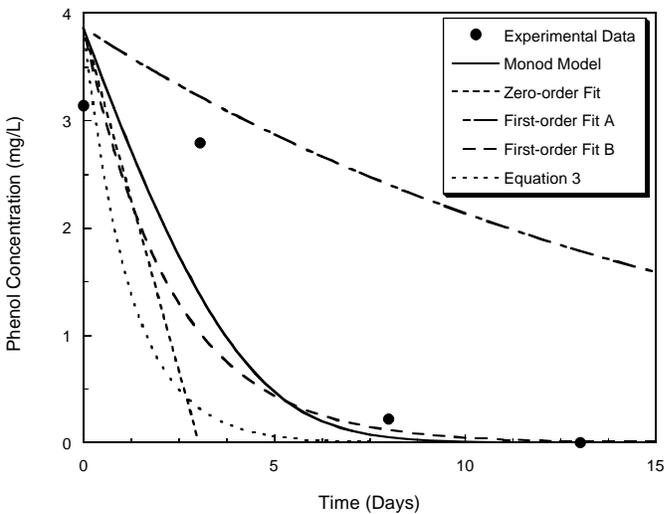


Figure 4: Comparison of the two first-order fits, the zero-order fit, and the Monod model for a starting concentration of 3.9 mg/L. The curve labeled equation (3) was obtained by using the fitted Monod constants from Figure 1 in the first-order approximation given by equation (3).

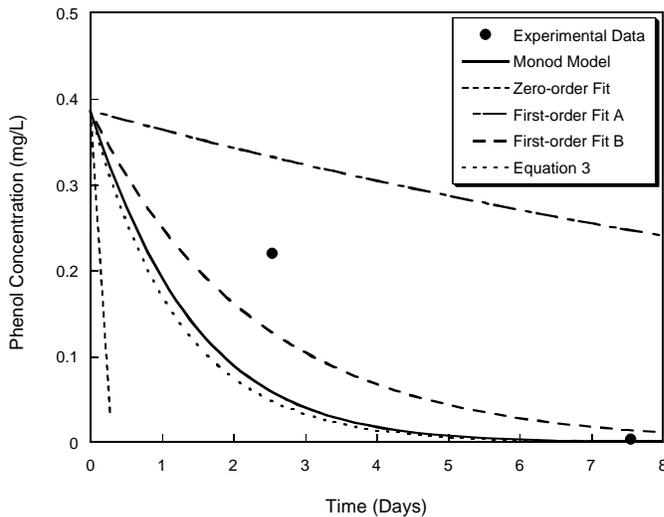


Figure 5: Comparison of the two first-order fits, the zero-order fit, the Monod model, and equation (3) for a starting concentration of 0.39 mg/L.

illustrates the simulation results for a starting concentration of 0.39 mg/L. In this case, the zero-order rate is far too fast. It is apparent that when the starting concentration is below 20% of  $K_S$ , the theoretical first-order rate expression obtained by using the Monod constants in equation (3) is the best approximation. Thus, if Monod parameters are used in a transport model with a first-

concentration of 3.9 mg/L. The plot shows that the prediction from fit A is excessively conservative for the lower concentrations. In contrast, the first-order rate from fit B provides a good estimate of the degradation profile. In particular, fit B predicts that the concentration would drop to half of its initial value seven times faster than fit A (1.6 vs. 12 days). Thus, using a first-order model to predict biotransformation for concentrations outside the range used to derive the rate constant could result in a significant error in estimated travel distance or clean-up time for a site. It is interesting to note that the zero-order profile also looks reasonable for values greater than  $K_S$  (1.7 mg/L). An error analysis shows that the zero-order rate is 50% too fast at the starting concentration and double the true rate at  $K_S$ . In contrast, the fit A rate is 75% too low at the start and 85% too low at  $K_S$ . The curve labeled equation (3) was obtained by using the fitted Monod constants (from Figure 1 and equation (2)) in the first-order approximation expression given by equation (3). The equivalent first-order rate,  $k$ , is  $0.82 \text{ day}^{-1}$ . For this concentration range and using the Monod constants, equation (3) substantially over-estimates the degradation rate. An important lesson here is that a fitted first-order rate such as fit B does not give the same results as would be estimated from the Monod parameters using equation (3). To further examine the approximations at the lower concentrations, Figure 5

order reaction term, equation (3) should be used to approximate the first-order rate only when the maximum concentration is below 20% of  $K_S$ .

## Discussion

Table 1 shows a summary of the Monod constants that have been measured for BTX compounds and the conditions under which they were obtained. The conditions of the experiments vary considerably, and this is reflected in the wide range of values obtained. Alexander and Scow (1989) discussed the factors that may cause rates to vary under different experimental conditions. The following summary is based on their discussion. One possible problem arises from comparing results for pure cultures with those for mixed aquifer populations because  $K_S$  and  $v_m$  describe the substrate utilization rate for a specific microbe adapted to the experimental conditions. In an aquifer, several species may be consuming the same substrate. In particular, very low values for  $K_S$  and  $v_m$  indicate adaptation to low substrate concentrations, whereas higher values represent adaptation to high concentrations (Slater and Lovatt, 1984). Another problem involves comparing rates for cultures suspended in liquid media with those attached to aquifer material. Diffusion into small pores and sorption can effectively compete for the substrate raising the apparent value of  $K_S$  and lowering the apparent  $v_m$  in aquifer material compared with liquid cultures (Alexander and Scow, 1989). When low concentrations exist in the fluid phase, the rate-limiting step may be desorption from the aquifer material. However, Kelly et al. (1996) recently compared Monod parameters obtained from suspended batch cultures and column studies and found no significant difference under the two conditions. Other possible effects on rates discussed by Alexander and Scow are: inhibition by other compounds present; limitations in electron acceptors and nutrients; low solubilities, biofilm diffusion limitations, and variation in microbial populations. Within the same aquifer Nielsen and Christensen (1994) found that microcosms containing sediment and water from eight locations in a 15 m x 30 m area gave rates for benzene that varied by a factor of four. Finally, temperature can be important when comparing lab and field rates. For aerobic bioreactors, the rate roughly doubles for each 10°C increase (Grady and Lim, 1980) although, for BTX compounds, Corseuil and Weber (1994) found that the rate tripled while Bradley and Chapelle (1995) found a 150% increase.

The six values of  $K_S$  for toluene in Table 1 range from 17.4 mg/L to below 0.1 mg/L and only one value exceeds 2 mg/L. Comparing the aqueous solubility of the toluene fraction in various petroleum products with concentrations of BTX observed in the field indicates that toluene concentrations may exceed this value in a significant number of cases. In a series of experiments where one part gasoline was rotated with 10 parts water, the concentrations of benzene and toluene averaged 59 and 33 mg/L, respectively (American Petroleum Institute, 1985) and toluene constituted 28% of the total BTX mass. For kerosene, diesel, and fuel oil, Dunlap and Beckman (1988) found that toluene was present at roughly twice the concentration of benzene. Salinitro (1993) summarized BTX data from 13 study sites and found that on average about 20% of the wells had total BTX concentrations greater than 5 mg/L and 7 out of the 13 sites had benzene concentrations greater than 2 mg/L. In addition, a database of LUFT sites recently compiled by the California State Water Resources Control Board (Rice et al., 1995a) lists the maximum benzene concentration as greater than 2 mg/L at 625 out of 1092 sites. From the relative

**Table 1:** Monod constants measured for aerobic degradation of BTX compounds.

Compound	Initial concentration, $S_0$ (mg/L)	Max. specific degradation rate, $\mu_m/Y$ (mg/mg-day)	Half-saturation constant, $K_S$ (mg/L)	Yield, $Y$ (mg/mg)	Materials and Methods	Reference
Toluene	1-100	9.9	17.4	-	Acclimated aquifer bacteria; saturated sediment microcosms; Hanes linear fit.	Alvarez et al. (1991)
Toluene	48.5	1.3-4.0	<0.100	0.5-1.5	Acclimated soil bacteria; unsaturated soil microcosms; linear fit of zero-order model.	Allen-King et al. (1994a)
Toluene	10.0	10.68	1.96	1.22	Two acclimated pure cultures; suspended cell lab microcosms; non-linear fit.	Chang et al. (1993)
Toluene	9.2	0.649	0.276	1.7	Mixed soil bacteria from contaminated site, enriched and acclimated; suspended cell lab microcosms; non-linear fit.	Kelly et al. (1996)
Toluene	3.0	0.493	0.655	0.426	Mixed aquifer bacteria; saturated flow columns; fit of 1-D reactive transport model.	MacQuarrie et al. (1990)
Toluene	1-30	0.34	0.044	0.17	Acclimated pure culture; suspended cell lab microcosms; non-linear fit	Robertson and Button, (1987)
Benzene	1-100	8.3	12.2	-	Same as in line 2	Alvarez et al. (1991)
Benzene	10.0	7.74	3.17	1.04	Same as in line 4	Chang et al. (1993)
Benzene	6.2	0.784	0.31	1.5	Same as in line 5	Kelly et al. (1996)
Benzene	10-110	3.84	20.0	-	Enriched soil bacteria from contaminated site; suspended cell lab microcosms; non-linear fit.	Goldsmith and Balderson, (1988)
<i>o</i> -Xylene	0.0205	3.03	0.0007	0.67	Acclimated mixed aquifer bacteria; suspended cell lab microcosms; non-linear fit.	Corseuil and Weber, (1994)
Mix of xylenes	6.4 (mean of two batches)	6.1	8.4	1.3	Same as in line 5	Kelly et al. (1996)

solubilities above, these sites should have toluene concentrations of 1.0 mg/L or more depending on the source type. Thus, toluene may be present in concentrations greater than  $K_S$  at potentially half of all sites and the use of first-order rates to describe the degradation would be questionable in these cases.

Models of intrinsic remediation generally assume a steady state in which the dissolved contaminants from a non-aqueous source are degraded within a fixed distance along a flow line. If the population of degrading microbes stabilizes at a constant value, then the concentration profile in ground water may be modeled using the one-dimensional transport equation with a biological reaction term:

$$D \frac{d^2 S}{dx^2} - v \frac{dS}{dx} - \frac{v_m}{q} \left[ \frac{S}{K_S + S} \right] = 0 \quad (9)$$

where  $D$  is the hydrodynamic dispersion coefficient ( $m^2/day$ ),  $S$  is the contaminant concentration,  $x$  is distance along a flow path (m),  $v$  is the average linear flow velocity (m/day),  $q$  is porosity (-), and  $v_m$  and  $K_S$  are defined as before. Note that  $v_m$  is the concentration loss of substrate per day in a unit volume of aquifer material. This is based on defining the biomass concentration,  $B$ , as mg biomass per unit volume of aquifer material. When the biomass concentration is defined in this manner, the reaction term must be divided by the porosity,  $q$ , as shown. If biomass is defined in terms of concentration in the fluid, the reaction term should not be divided by  $q$ .

Parlange et al. (1984) presented an analytical solution to equation (9) for the case when the source is specified as a constant concentration boundary and dispersion is neglected:

$$\frac{vq}{v_m} \left[ K_S \ln \left( \frac{S_0}{S(x)} \right) + S_0 - S(x) \right] = x, \quad (10)$$

where  $S_0$  is the concentration at the source. To use this solution with a spreadsheet, create a column with a range of concentrations,  $S$ , and use the formula to compute the corresponding expected distance to reach a given concentration. Parlange et al. (1984) show that longitudinal dispersion is mainly important near the advancing front of a plume. Thus, in the case of a steady-state plume, the effect of longitudinal dispersion can be neglected. In addition, when the source of a plume is wide in the direction perpendicular to flow, transverse dispersion is also minimal. Thus equation (10) is an appropriate choice for modeling Monod degradation in a steady-state plume with a wide source.

Figure 6 illustrates the application of equation (10) to a field site in Pensacola, FL that is contaminated with creosote compounds. The site is at steady state and has a 100 m wide by 20 m deep non-aqueous source so that the effect of transverse dispersion is minimal. The figure shows phenol data from the site together with the results of two formulations of a one-dimensional transport model: one incorporating a first-order transformation rate and one incorporating Monod kinetics. To obtain the first-order rate constant we plotted the natural log of concentration versus distance and obtained the best fit regression line (Figure 6a). The slope of this line corresponds to coefficient,  $k$ , in the solution for advective transport with first-order kinetics given by  $S(x) =$

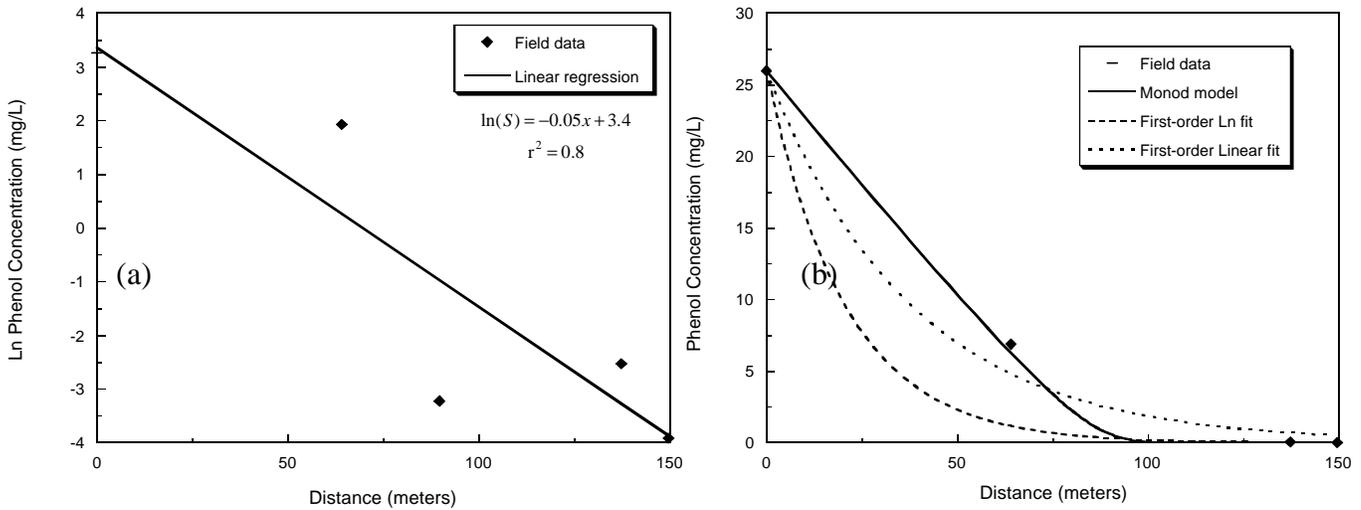


Figure 6: Comparison of field data from a creosote-contaminated site in Pensacola, FL to results from three reactive transport models assuming a flow velocity of  $v = 1.0$  m/day (Bekins et al., 1993). (a) Fitting a first-order decay constant in semi-log space gives  $k = 0.048$  day<sup>-1</sup>. (b) The solid line was generated using fitted Monod parameters from Bekins et al. (1993):  $v_m = 0.337$  mg/L-day, and  $K_S = 1.33$  mg/L in equation 10. The long-dashed line, labeled “First-order Ln fit”, has a first-order decay constant obtained from the semi-log plot in (a). The short-dashed line, labeled “First-order Linear fit”, is the best first-order kinetics fit to the data in linear space.

$S_0 \exp(k \cdot x/v)$  (Wiedemeier et al., 1995). Figure 6b shows a comparison of the two first-order fits to the analytical solution for Monod kinetics. The parameter values of the fits were obtained by fitting the field data to first-order kinetics models in semi-log and linear space. The Monod model clearly does a better job of describing the field concentration profile. This is because the maximum concentration found at the site is more than an order of magnitude greater than the half-saturation constant ( $K_S = 1.33$  mg/L).

Models are often used to predict the time until the concentration of a contaminant reaches some minimum concentration, usually the Maximum Concentration Limit (MCL) set by the U.S. Environmental Protection Agency. A comparison of the three models in Figure 6b shows that estimates for the clean-up time of a site are dependent on the correct model choice. For example, the times associated with a 95% concentration decrease (to 1.3 mg/L) are 62, 85, and 114 days for the three models. Assuming the Monod model is correct, the estimates based on the two first-order models are either 27% too fast or 34% too slow. In general, time estimates based on first-order models will be quite different from those based on Monod models.

To avoid misusing first-order models the following steps should be followed when determining biotransformation rates for use in natural attenuation models. First, obtain concentration data from at least four wells with values spanning two orders of magnitude along a flow line. Next, verify that the same electron accepting process prevails over the flow path to be modeled (see Wiedemeier et al. (1995) for a discussion). If the dispersivity is small or the non-aqueous source is large perpendicular to the flow direction, then plot the concentration versus distance in both linear and semi-log space. If the data lie along a line in linear space and are concave down in semi-log space then Monod degradation kinetics apply and equation (10) may be used to estimate the biodegradation kinetics. A rough least-squares fit may be performed with a spreadsheet program

by using the distances for the measured concentrations and the  $x$  values computed from equation (10). For BTX compounds, try  $K_S$  values ranging from 0.01-10.0 mg/L. Note that equation (10) will also model a first-order rate with less than a 10% error if  $K_S$  is set to ten times the maximum concentration present.

If dispersivities are large, it is important to remember that the combined effect of Monod degradation kinetics and dispersion may appear to follow a first-order degradation profile. Thus, in this case, it is crucial to use a reliable method to separate these two effects. Wiedemeier et al. (1995) describe an analytical method of using a conservation tracer to correct the data for the effects of dispersion. Unfortunately, this method is accurate for first-order but not for Monod degradation kinetics. Thus, when contaminant concentrations are greater than 1 mg/L, a numerical model with Monod kinetics is required to distinguish between the effects of dispersivity and degradation.

## Summary and Conclusions

We have raised several issues regarding the modeling of degradation rates using first- and zero-order approximations to Monod kinetics. The basic problem is that these approximations are valid over only part of the concentration range of BTX compounds that may be present in a contaminated aquifer. The common assumption of a first-order rate expression for BTX degradation is questionable because most of the published half-saturation constants are lower than the maximum concentrations observed at the majority of field sites. In general, the use of first-order approximations should be questioned if the maximum concentration of benzene is over about 1 mg/L or total BTX is greater than 5 mg/L. However, if data are used to compute a first-order rate for a site, the highest and lowest concentrations used in the fit should be presented. In addition, first-order rate constants should not be compared when the concentration ranges used to obtain the rates differ significantly. Moreover, a first-order rate obtained by fitting a line on a semi-log plot should be evaluated by plotting the corresponding exponential decay function together with the data on a linear plot. Finally, first-order rates should not be used for predictions outside the concentration range where they were obtained unless the condition for the use of a first-order approximation has been verified.

The advantages of correctly representing the kinetic dependence on the rate-limiting substrate are many. In the short term, the potential for erroneous predictions of natural attenuation potential is minimized. In the larger view, the use of the correct rate expression is the first step in ultimately understanding the many processes that contribute to the observed biodegradation rates in the field.

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