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COMPARING ZERO- AND FIRST-ORDER APPROXIMATIONS TO THE MONOD MODEL

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ABSTRACT: First-order kinetics can be a poor representation of biotransformation rates in contaminated aquifers. A quantitative expression of the relative error in the first- and zero-order approximations shows that significant errors occur outside the valid range of approximation. The problems that arise are illustrated by a comparison of laboratory data to simulation results using first- and zero-order approximations and Monod kinetics. In particular, compared to Monod kinetics, first-order approximations predict slower biotransformation rates for concentrations below the half-saturation constant, and faster rates above the half-saturation constant. A literature survey of maximum field concentrations of benzene and measured aerobic half-saturation constants suggests that an assumption of first-order degradation kinetics is not necessarily valid, and use of a zero-order assumption or a full solution may be more appropriate. A solution for steady-state, one-dimensional, advection with Monod degradation kinetics is described and applied to groundwater concentration data. The results indicate that Monod kinetics more closely models the aerobic biotransformation of benzene at the study site.

INTRODUCTION

Evaluation of the bioremediation potential of a field site requires 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, including the Monod expression, and its first- and zero-order approximations. Of these expressions, 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 analysis of the data using the first-order approximation is convenient, its 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.

Comparing measurements of the half-saturation constant for benzene with maximum observed concentrations at contaminated sites suggests that first-order models are probably widely misapplied. This paper explores the problems that arise when first-order rates are fitted to a data set and then used to predict concentrations outside the range of the data. Theoretical error analyses together with results from numerical simulations are used to illustrate that substantial errors can occur when first-order approximations are misapplied. Significantly better

results can be obtained by using an analytical solution for advective transport with Monod degradation kinetics.

Theoretical Approximation Error. 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 constant temperature were presented by Monod (1949). Simkins and Alexander (1984) presented a simplified equation for no-growth conditions:

$$\frac{dS}{dt} = -v_m \frac{S}{K_S + S} \quad (1)$$

where S is the substrate concentration (mg/L); t is time (day); v_m is the maximum substrate utilization rate (mg/L•day); and K_S is the half saturation constant (mg/L).

When S is several times smaller than K_S , (1) may be approximated by a first-order equation:

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

Frequently the Monod parameters (v_m/K_S) in (2) are combined into a first-order rate constant, k (day^{-1}). The value of k is obtained by finding the slope of the best fit line on a plot of log concentration versus time.

When S is several times greater than K_S , the rate is independent of the concentration and (1) is approximated by a zero-order equation:

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

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.

A relative error for each approximation can be obtained by subtracting (2) or (3) from (1), then dividing by (1), and taking the absolute value. The errors associated with the first- and zero-order approximations, respectively, are:

$$\bar{e}_1 = \frac{S}{K_S} \times 100\%; \quad (4) \quad \text{and} \quad \bar{e}_0 = \frac{K_S}{S} \times 100\%. \quad (5)$$

The result in (4) shows that, for the first-order approximation, the error will be small when S is much less than K_S . For example, the error is less than 10% when $S < 0.1K_S$. However, if this assumption is violated, the error quickly becomes quite large; if $S = 10K_S$, the error will be an impressive 1000%. The zero-order case is opposite. In particular, the error is less than 10% whenever $S > 10K_S$ and greater than 1000% when $S < 0.1K_S$. Clearly, the relative values of S and K_S have a significant effect on the approximation error.

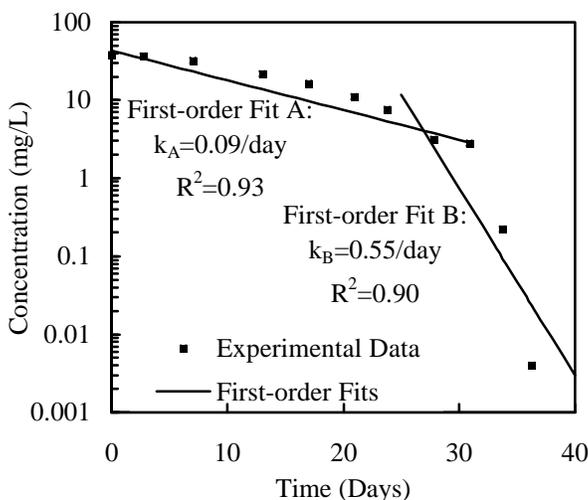


FIGURE 1. Laboratory phenol degradation data on a semi-log scale with two lines, denoted A and B, fit by linear regression to the high and low concentration ranges.

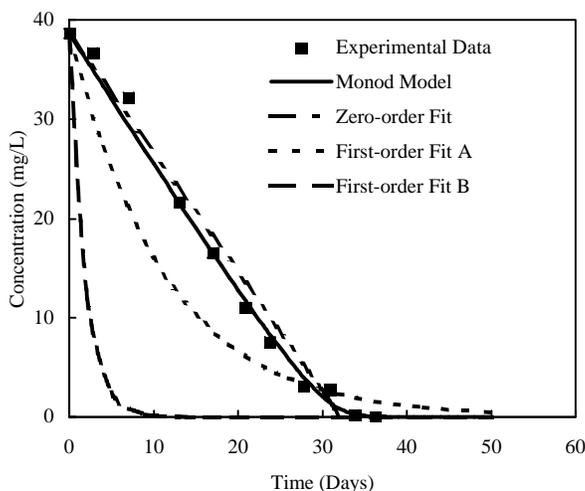


FIGURE 2. Phenol data with results from four models: Monod; first-order fit A; first-order fit B; and the zero-order fit.

Alternatively, fit B might be chosen based on a data set in which the higher concentrations are missing. For example, if a batch microcosm was prepared with a starting concentration of 3.0 mg/L a partial data set would be obtained and fitted with the rate shown in fit B.

The zero-order approximation and Monod model both provide a better fit to the data (Figure 2). The zero-order rate is best for concentrations above 3.0 mg/L which is consistent with our error analysis. Both the first-order fits A and B predict rates that are too rapid for concentrations above 3.0 mg/L. This result

Graphical Evaluation of the Approximations. Comparison of a Monod model and its approximations to methanogenic batch microcosm data provides an example of how violation of the necessary assumptions may produce poor results (Figure 1). The microcosm was prepared with sufficient nutrients so that phenol was the rate-limiting substrate. Because of the low growth of the methanogenic consortia, the transformation can be described by (1). Using non-linear regression of (1) on the full data set we obtained the Monod parameters, $v_m = 1.39$ mg•L/day and $K_S = 1.7$ mg/L.

If a first-order rate applies, the log concentration versus time data should fall along a single line. Instead, they form a concave-down profile, precluding a reasonable linear fit. In general, a concave down profile of log concentration versus time is evidence that a Monod model applies. To force a linear fit, one might choose to fit the higher concentration data (fit A), the lower concentration data (fit B), or all the data.

Fit A might be chosen on the basis of an assumption that the last two data points have larger associated analytical

illustrates the problems that arise when trying to fit a first-order model to concentrations that are significantly greater than the half-saturation constant. If a simulation with a starting concentration of 3.0 mg/L is made, the first-order rate from fit B will be reasonable but the rate from A will be much too slow. This is typical of the errors involved in using a first-order fit from high concentrations to predict the rate for low concentrations. The intermediate strategy of performing a fit to the entire data set gives a poor R^2 value and exhibits the problems of both fits A and B. Like fit A, the rate will be too slow for the low concentrations; and, like both A and B, the rate will be too fast for the high concentrations.

DISCUSSION

Published K_S values for benzene compiled by Bekins et al. (*in review*), ranged from 20.0 to 0.31 mg/L, with two of the four values below 4 mg/L. A recent survey of contaminated sites in California (Rice et al., 1995) revealed that half have benzene concentrations in excess of this value, making application of a first-order model questionable.

TABLE 1. Parameter values for site 05026 determined by first-order and Monod fits.

Parameter	Value	R^2
k_1 (day ⁻¹)	0.060	0.990
k_2 (day ⁻¹)	0.032	1.000
v_m/v (mg/L•m)	0.035	0.999
K_S (mg/L)	0.367	

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. For a steady-state plume, Parlange et al. (1984) showed that the effect of longitudinal dispersion can be neglected. Transverse dispersion is also minimal when the source of a plume is wide in the direction perpendicular to flow and the concentration profile may be modeled as steady-state one-dimensional advection with biotransformation:

$$v \frac{dS}{dx} - v_m \left[\frac{S}{K_S + S} \right] = 0 \quad (6)$$

where v is the average linear flow velocity (m/day), x is distance along a flow path (m), and S , v_m , and K_S are defined as before. Parlange et al. (1984) presented an implicit analytical solution to (6) for the case when the source is specified as a constant concentration equal to S_0 (mg/L):

$$\frac{v}{v_m} \left[K_S \ln \left(\frac{S_0}{S(x)} \right) + S_0 - S(x) \right] = x. \quad (7)$$

A former gasoline station (Figure 3) in Santa Clara County, California (site number 05026 in the Plume-a-Thon database; Rice et al., 1995), had four wells with benzene concentrations ranging from 1.20 mg/L to below detection

over a distance of 200 m (Petryna, 1994), from which Monod and first-order rate parameters were calculated (Table 1). Biotransformation curves (Figure 4) were generated using the values in Table 1. Even though the first-order approximation closely fit the data on a semi-log plot, a plot of the first-order degradation profile in linear space shows that the rate (k_1) is overestimated. If only the first two data points are used in a first-order fit, the rate (k_2) is underestimated at the lower concentrations. Because the calculated K_S from the field data set is significantly smaller than the starting concentration, the Monod model provides a better fit to the data than either first-order approximation. The Monod model is capable of

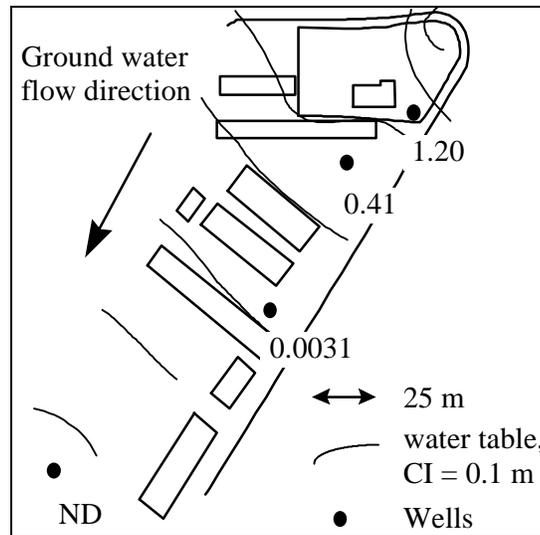


FIGURE 3. Location of sampling wells (with benzene concentrations in mg/L) and water table contours at a former gasoline station.

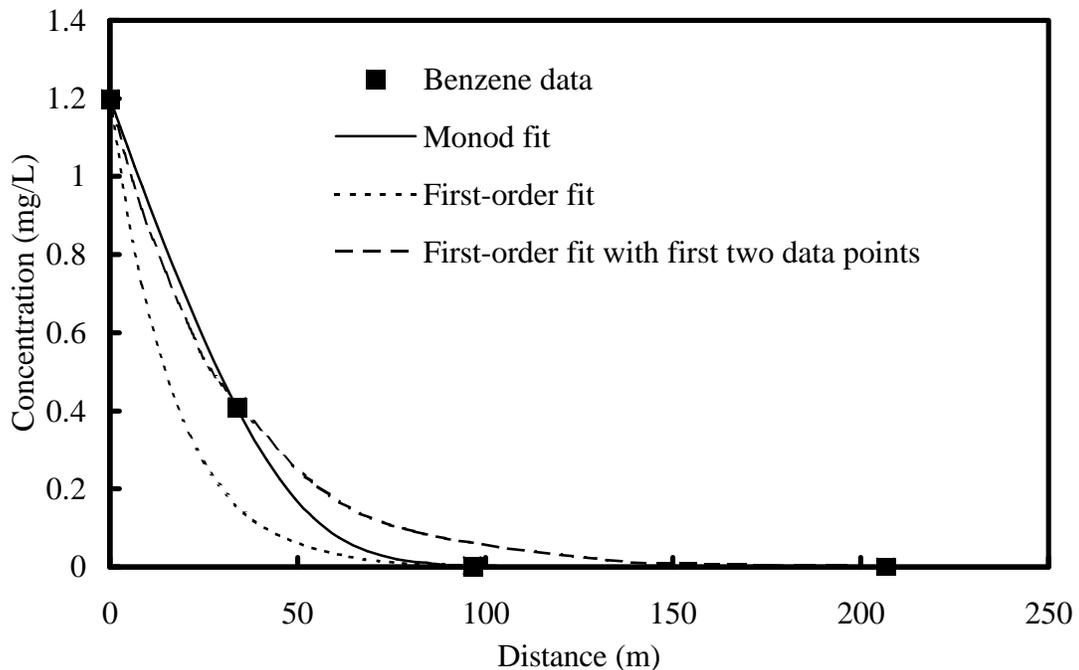


FIGURE 4. Benzene data with results from Monod and first-order models.

reproducing the zero-order nature of the data above K_S and the first-order nature below K_S .

SUMMARY AND CONCLUSIONS

The first-order approximation of the Monod model may not be appropriate under many conditions. First-order approximations give erroneous results when fitted to data outside the range for which they are valid. Especially serious errors result when first-order rates are extrapolated beyond the measured data. It is necessary to assess which model is appropriate by determining K_S and comparing it to the maximum S . First-order models should not be used if K_S is less than the maximum S . In this case, either the zero-order model or the full Monod model should be used. An analytical solution for advection with Monod degradation provides a simple alternative to analytical solutions based on first-order rates.

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