Conf-9206116--4

PNL-SA--20622

DE92 019125

EFFECTS OF LAG AND MAXIMUM GROWTH IN CONTAMINANT TRANSPORT AND BIODEGRADATION MODELING

B. D. Wood
C. N. Dawson

June 1992

Paper presented at
University of Colorado International
Conference on Computational Methods
in Water Resources
June 9-12, 1992
Denver, Colorado

Work supported by
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

EFFECTS OF LAG AND MAXIMUM GROWTH IN CONTAMINANT TRANSPORT AND BIODEGRADATION MODELING

Brian D. Wood
Pacific Northwest Laboratory, Richland, Washington U.S.A.

Clint N. Dawson
Department of Mathematical Sciences, Rice University, Houston, Texas U.S.A.

Abstract: The effects of time lag and maximum microbial growth on biodegradation in contaminant transport are discussed. A mathematical model is formulated that accounts for these effects, and a numerical case study is presented that demonstrates how lag influences biodegradation.

1 Introduction

The contamination of groundwater supplies by possibly toxic compounds has become a problem of great concern in recent years. Under normal soil conditions, substantial amounts of organic compounds can be removed by natural biodegradation when sufficient nutrients are present [1, 2]. Furthermore, natural biodegradation can be enhanced by the introduction of dissolved oxygen and other nutrients into nutrient-depleted areas. This process, called *in-situ* biorestoration, has shown tremendous potential as a cost-effective remediation technology in recent field and laboratory studies (e.g., [3]).

Several mathematical models of *in-situ* biodegradation have been proposed that describe the transport and interaction of substrates, nutrients, and microorganisms in the subsurface (e.g., [4, 5, 6]). In these models, transport is assumed to be linear; however, different biodegradation models are assumed. Recently, the first author studied the effects of microbial lag and maximum growth on biodegradation, and has proposed a new mathematical model for describing the reaction kinetics that generalizes the Monod kinetic equations.

In order to quantify the effects of time lag and maximum growth, the kinetics model has been incorporated into a simulator developed by the last author and Mary F. Wheeler. In this paper, we describe the mathematical model including lag and maximum growth and present some preliminary results which demonstrate the effects on biodegradation. A more intensive numerical study of these effects, and comparison to laboratory experiments, will be presented in a later paper.

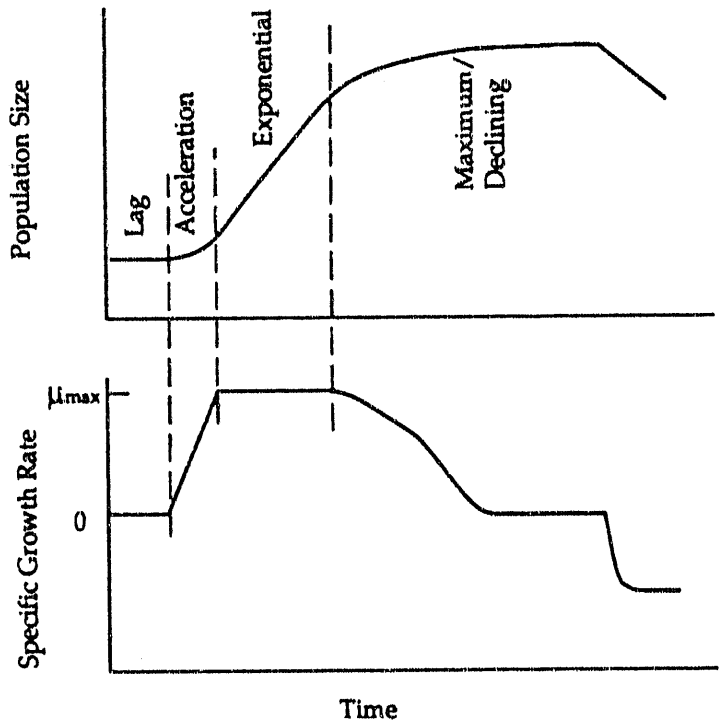

Figure 1: Hypothetical growth curve for microorganisms

2 Description of kinetics

Over the last few years a variety of models have been proposed to describe the growth of microorganisms in porous media that have addressed both the proper microbial kinetics to be employed for a variety of situations [4, 5, 7, 8], as well as issues concerning the effects of the physical distribution of the microorganisms [6, 9, 10]. Despite these developments, there are still many phenomena pertaining to microbial growth in porous media that are not adequately accounted for. One such phenomenon is the "lag phase" (or "lag period"), defined as a period of time during which no microbial metabolism of a newly encountered substrate occurs because of metabolic limitations.

Figure 1 shows a hypothetical growth curve for microorganisms in porous media [11]. Although this curve is similar to a conventional batch growth curve, it has been assumed by modelers to apply to growth in "open" porous media systems (e.g., [4, 5, 7]), and has been observed in laboratory column experiments. For the purposes of analysis, the growth curve can be divided into separate stages that need to be included in the expression of the microbial kinetics. These stages are 1) the lag phase, 2) the acceleration phase, 3) the exponential phase, and 4) the maximum/declining stage.

The occurrence of a lag phase is usually attributed to the need for the microorganism to produce the enzymes necessary for metabolism of the new substrate, but can also be a result of cell damage (other than enzymatic) or stress, the need to reduce components toxic to the cell in the environment, and a host of other environmental and cellular factors [12]. Because contaminants can often be refractory, it is not unusual for microorganisms to exhibit lag times of months

or more for some of these compounds [13]; thus, accounting for microbial lag times may be particularly important for simulating bioremediation of exogenous substances. The acceleration phase is a transition between the lag phase and exponential growth. During this period the metabolic pathways needed to degrade a given substrate increase to their full capacity, at which point the organisms are in the exponential growth phase. The microbial population will eventually reach a plateau for one of two reasons. First, growth may become substrate- or electron acceptor-limited; this has generally been accounted for in numerical models by using a Monod-type description of substrate uptake. The second possibility is that microbial mass may become so dense that the production of metabolic exotoxins or spatial limitations inhibit further growth. In this case, the microbial mass still removes substrate from the system for maintenance energy purposes; i.e., a certain amount of substrate is required to provide the cell with energy even where there is no growth. This mechanism has generally not been considered in previous bioremediation models. Limiting the total microbial mass, however, may be important in bioremediation modeling; in models that do not limit the total microbial mass, the concentration of microorganisms may reach unrealistically high values where substrate and electron acceptors are abundant.

The approach taken here is one that assumes that a macroscopic description of microbial growth is valid [10, 14]. In order to account for the processes listed above that may affect microbial growth in porous media, the following set of equations are suggested for the growth of a single, non-transported microbial species (X) with the availability of one substrate (S) and one electron acceptor (O) (X, S, and O in units of $[M/L^3]$):

$$\frac{\partial X}{\partial t} = X\left(\frac{\mu S}{S+K_S}\right)\left(\frac{O}{O+K_0}\right)\lambda - bX, \tag{1}$$

where

$$\lambda = \begin{cases} 0, & t < t_L, \\ \left[\frac{t-t_L}{t_E-t_L}\right]\left[1-\frac{X}{X_m}\right], & t > t_L, \end{cases} \tag{2}$$

$$\frac{\partial S}{\partial t} = B_S(X,S,O) \equiv -\frac{-\mu\lambda X}{Y}\left(\frac{S}{S+K_S}\right)\left(\frac{O}{O+K_O}\right), \tag{3}$$

$$\frac{\partial O}{\partial t} = B_O(X,S,O) \equiv -\frac{f\mu\lambda X}{Y}\left(\frac{S}{S+K_S}\right)\left(\frac{O}{O+K_0}\right). \tag{4}$$

Variables not previously described in the text are defined as follows: μ=the maximum specific growth rate $[1/T]$; K_S=the half-saturation constant for the substrate $[M/L^3]$; K_O=the half-saturation constant for the electron acceptor; b=maintenance energy/microbial decay coefficient $[1/T]$; Y=yield coefficient

for microbial growth; X_m=maximum limiting microbial concentration $[M/L^3]$; t_L=the lag time (starting from the time at which initial contact with substrate is made); t_E=the time when exponential growth begins (starting from the time at which initial contact with substrate is made); f=mass of electron acceptor used per unit mass of substrate degraded.

In the model, we assume there is no transport of microorganisms, although this poses no difficulty for the numerical algorithm. This is a reasonable assumption for many subsurface systems because a large fraction of the subsurface organisms present in both native and contaminated sites are attached to solid surfaces [15, 16].

The expression for λ above is essentially the combination of the logistic growth model which has been used for some time to describe microbial growth where maximum concentration limitations occur [17], and the acceleration phase model proposed in [18]. During the initial period of contact with a substrate (assuming that the microbial concentration is small compared to X_m) the first term in brackets in (2) dominates the expression. At times greater than t_E, this term is equal to unity; if the concentration of microorganisms is also much less than X_m, then (1) reduces to a strictly Monod-kinetics dominated model. If the concentration of microorganisms gets large enough, the second term in brackets in (2) dominates the expression, and microbial growth is limited even in the presence of excess substrate and electron acceptor.

3 Numerical method

The transport of substrate component is described by

$$\phi R_S \frac{\partial S}{\partial t} - \nabla \cdot (D\nabla S - uS) = \phi R_S B_S(X, S, O). \tag{5}$$

For dissolved oxygen,

$$\phi \frac{\partial O}{\partial t} - \nabla \cdot (D\nabla O - uO) = \phi B_O(X, S, O). \tag{6}$$

In these equations, ϕ is porosity, R_S is the retardation factor due to adsorption of substrate, and D is the hydrodynamic diffusion/dispersion tensor. Note that we have assumed a linear Freundlich model for adsorption. The function u represents the Darcy velocity, which satisfies

$$u = -K\nabla h, \tag{7}$$

$$\nabla \cdot u = 0, \tag{8}$$

where K represents hydraulic conductivity and h hydraulic head.

In our numerical simulator we first approximate the Darcy velocity u and hydraulic head h using a mixed finite element method applied to (7) and (8).

To solve the system of transport and biodegradation equations, given by (1), (5), and (6), we employ a time-splitting technique. At each time step, we first approximate transport using a finite element-modified method of characteristics to solve (5) and (6) with right-hand sides set to zero. The approximations generated from this step are used as initial data for the system of ordinary differential equations given by (1), (5), and (6) with D and u set to zero. Here we use a second-order, explicit Runge-Kutta method and take small time steps, depending on the stiffness of the system.

This time-splitting approach is described in more detail and analyzed in [19]. Numerical studies of *in-situ* biorestoration under the effects of variable hydraulic conducitivity and variable adsorption can be found in [20]. The analysis of this method shows that for sufficiently smooth solutions, the L^2 norm of the error at any time level is $\mathcal{O}(h^2 + \Delta t)$.

4 Experimental results

To demonstrate the effects of lag on biodegradation, we considered flow through a homogeneous medium with dimensions 100 meters by 10 meters. A constant x-velocity of 0.25 meters/day was assumed, with y-velocity zero. We assumed an initial microbe concentration (X_0) of 0.0015 mg/l. We also assumed an initial concentration of dissolved oxygen of 10 mg/l. At the inflow boundary we placed a substrate pulse of width 5 meters. We assumed inflow of oxygen behind the pulse. The longitudinal mixing length was 0.25 meters, and porosity was 0.3. 220 uniform grid blocks in the x-direction were used in the simulation, with a transport time step of .2 days, and a reactive time step of 0.001 days. The kinetic parameters were determined from laboratory experiments. The values used were $\mu = 0.582$, $f = 1.5$, $Y = 0.388$, $K_S = 0.1$, $K_O = 0.01$, and $b = 0$. In the definition of λ, $t_E = t_L + 1.5$ days, and $X_m = 50$ mg/l.

If Figure 2, we plot normalized substrate concentrations along the line $y = 5$ meters at 80 days for various lag times. The lag times used were 0, 20, and 30 days. We compare these results to a non-reactive solution. The amount of biodegradation which can occur depends on the ratio of the lag time to the "residence time" of the subtrate; i.e., the amount of time substrate is present in any given location. This quantity is plotted in Figure 3 for $t_L = 30$ days. As demonstrated by Figure 2, the effects of lag on the amount of substrate in the system can be substantial. For lag times close to the maximum residence time, little biodegradation has occurred.

5 Conclusions and future work

Based on experimental data and numerical simulations, the effects of lag and maximum microbial growth in biodegradation appear to have substantial influence on the efficiency of the bioremediation process. We are currently in the

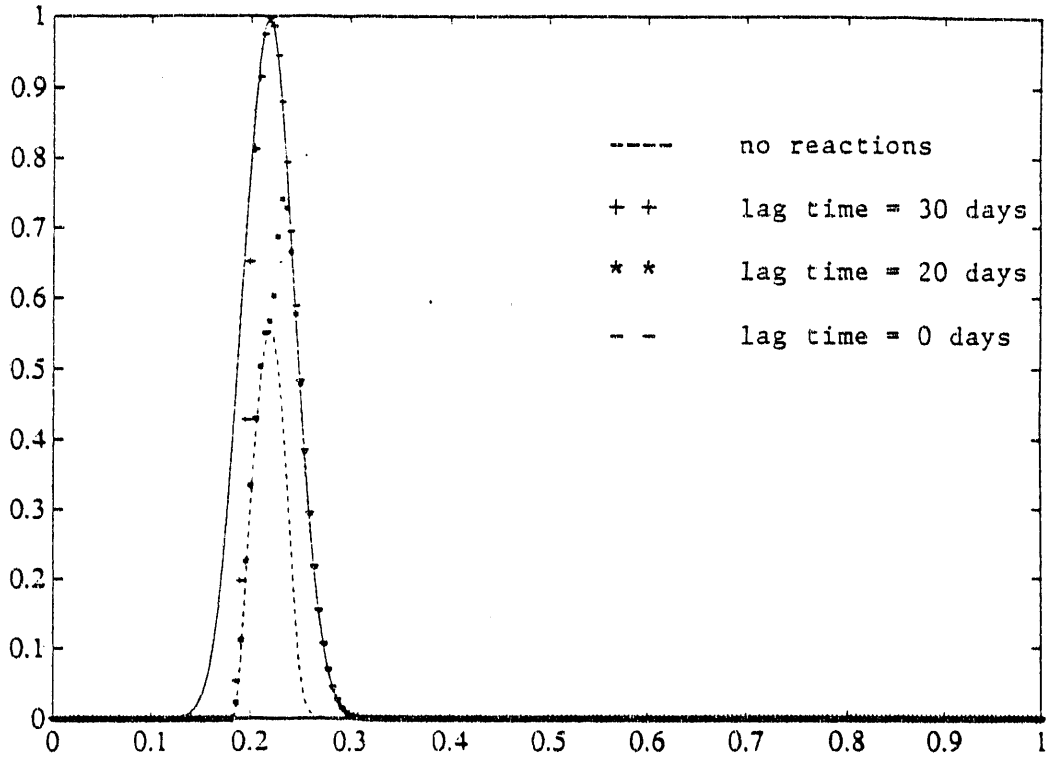

Figure 2: Normalized substrate concentrations vs. normalized distance for different lag times

process of incorporating more general reaction kinetics into our model, including multiple substrates with multiple lag times. The results of this research will be reported in a later paper.

Acknowledgments: This work was supported in part by the Office of Technology and Development, VOC Arid Site Integrated Demonstration Program, United States Department of Energy under contract DE-ACO6-76RLO 1830.

References

[1] Thomas, J. M., M. D. Lee, P. B. Bedient, R. C. Borden, L. W. Canter, and C. H. Ward, *Leaking underground storage tanks: remediation with emphasis on* in situ *biorestoration*, Environmental Protection Agency, 600/2-87,008, January, 1987.

[2] United States Department of Energy, *Site-directed subsurface environmental initiative, five year summary and plan for fundamental research in subsoils and in groundwater, FY1989-FY1993*, DOE/ER 034411, Office of Energy Research, April 1988.

[3] Raymond, R. L., V. W. Jamison, and J. D. Hudson, *Final report on beneficial stimulation of bacterial activity in ground water containing petroleum*

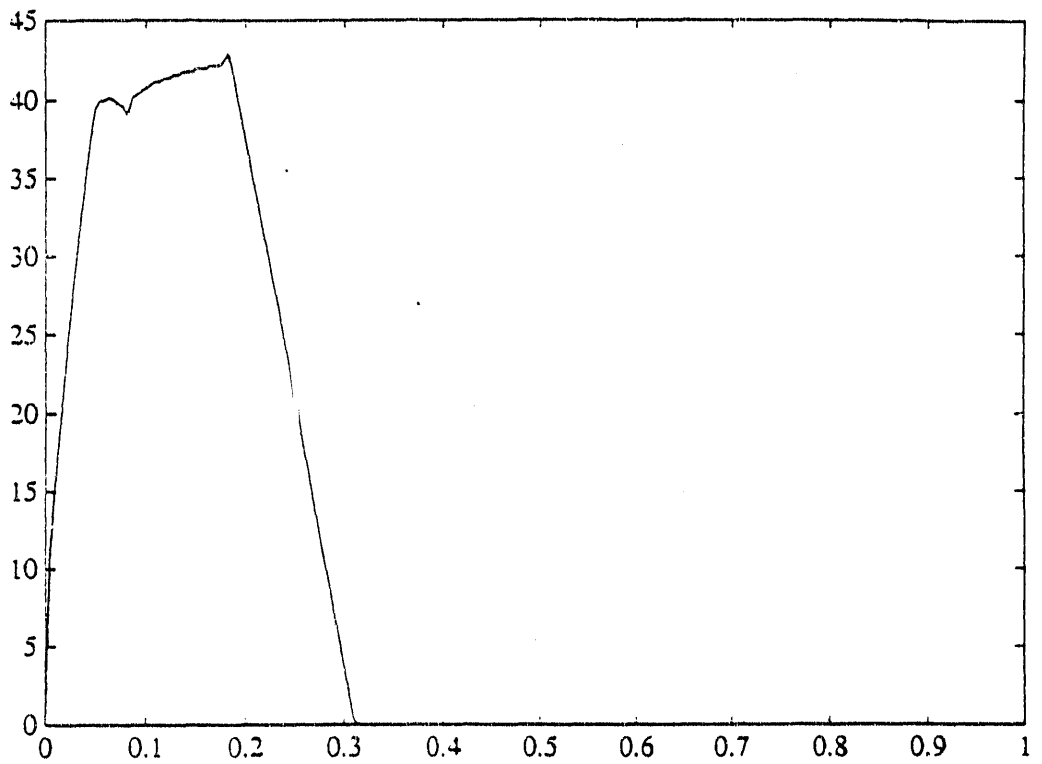

Figure 3: Residence time (days) vs. normalized distance

products, Committee on Environmental Affairs, American Petroleum Institute, Washington, D. C., 1975.

[4] Borden, R. C. and P. B. Bedient, *Transport of dissolved hydrocarbons influenced by oxygen-limited biodegradation 1. Theoretical development*, Water Resour. Res., 22, 1973-1982, 1986.

[5] Kindred, J. S. and M. A. Celia, *Contaminant transport and biodegradation 2. Conceptual model and test simulations*, Water Resour. Res., 25, 1149-1159, 1989.

[6] Molz, F. J., M. A. Widdowson, and L. D. Benefield, *Simulation of microbial growth dynamics coupled to nutrient and oxygen transport in porous media*, Water Resour. Res., 22, 1207-1216, 1986.

[7] Sykes, J.F., S. Soyupak, and G.J. Farquhar, *Modeling of leachate organic migration and attenuation in groundwaters below sanitary landfills*, Water Resour. Res., 18, 135- 145, 1982.

[8] Bouwer, E.J., and P. McCarty, *Modeling of trace organics biotransformation in the subsurface*, Ground Water, 22, 433-440, 1984.

[9] Corapcioglu, M.Y., and A. Haridas, *Transport and fate of microorganisms in porous media: a theoretical investigation*, J. Hydrol., 72, 149-169.

[10] Baveye, P, and A. Valocchi, *An evaluation of mathematical models of the transport of biologically reacting solutes in saturated soils and aquifers*, Water Resour. Res., 25, 1413-1421, 1989.

[11] Bull, A. J., *Microbial growth*, in Companion to Biochemistry, p. 415, Longman, London, 1974.

[12] Bartford, J.P., N.B. Pamment, and R.J. Hall, *Lag phases and transients*, in Mathematical Models in Microbiology, CRC Press, Boca Raton, Florida, 1982.

[13] Bouwer, E.J., and P. McCarty, *Transformations of 1- and 2-carbon halogenated aliphatic organic compounds under methanogenic conditions*, Appl. Environ. Microbiol., 45, 1286-1294, 1983.

[14] MacQuarrie, K.T.B., I.A. Sudicky, and E.O. Frind, *Simulation of biodegradable organic contaminants in groundwater, 1. Numerical formulation in principal directions*, Water Resour. Res., 26, 107-222, 1990.

[15] Zobell, C.E., *The influence of solid surface upon the physiological activities of bacteria in sea water*, J. Bacteriology, 33, 86, 1937.

[16] Harvey, R.W, R.L. Smith, and L. George, *Effect of organic contamination upon microbial distributions and heterotrophic uptake in a Cape Cod, Mass. Aquifer*, Appl Environ. Microbiol., 48, 1197-1202, 1984.

[17] Lynch, J.M., and J.E. Hobbie, *Microbial population and community dynamics*, in Microorganisms in Action: Concepts and Applications in Microbial Ecology, Blackwell Scientific, Oxford, 1988.

[18] Kono, T., *Kinetics of microbial cell growth*, Biotechnology and Bioengineering, 10, 105-131, 1968.

[19] Wheeler, M. F. and C. N. Dawson, *An operator-splitting method for advection-diffusion-reaction problems*, MAFELAP Proceedings VI, J. A. Whiteman, ed., Academic Press, 463-482, 1988.

[20] Chiang, C. Y., C. N. Dawson, and M. F. Wheeler, *Modeling of* in-situ *biorestoration of organic compounds in groundwater*, to appear in Transport in Porous Media.

END

DATE
FILMED
10/15/92