

Modeling transport and biodegradation of BTX compounds in saturated sandy soil

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Abstract

Numerical models have been developed using finite difference and orthogonal collocation methods to simulate one dimensional transport with time-dependent pore water velocity. The modeling process includes sorption given by linear isotherm and biodegradation given by a variety of kinetics such as first-order, zero-order, Monod, non-growth associated Monod (Michaelis–Menten), Haldane and many other inhibitory and non-inhibitory kinetics. A number of initial and boundary conditions such as Dirichlet's, Neuman's, mixed, decaying, etc. have been modeled. The method of finite difference (for first order/zero order model only) and the method of orthogonal collocation (for all kinetics models) have been used to solve the governing transport equation. Numerical solutions have been verified with existing analytical solutions for special cases. Three models (first-order and/or zero-order, non growth associated Michaelis Menten, and Monod) have been inverted using a Gauss–Marquardt–Levenberg algorithm to assess the transport parameters. The models have been used to simulate one dimensional transport of BTX compounds in a pilot scale sand tank model. The data have been found to fit to all three kinetic models with acceptable coefficient of determination (R^2) and parameter values. The high concentration data have been found to fit better to the Michaelis Menten and the Monod models than the first order/zero order model. © 1997 Elsevier Science B.V.

1. Introduction

Groundwater contamination by organic compounds represents a serious potential public health problem. Benzene, Toluene and Xylene (BTX) compounds are the main constituents of gasoline and their presence in groundwater is very common because of hydrocarbon spill and leakage of storage tanks. Leaking underground storage tanks

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(USTs) are a major source of groundwater contamination by petroleum hydrocarbons. Approximately 75,000 to 100,000 tanks out of total 1.4 million in the U.S.A. are leaking [1]. There were approximately 90,000 confirmed releases for the two years of 1989 and 1990 [2].

Bioremediation is the most widely used technique among all the currently employed methods for treating BTX contaminated soil and groundwater [3]. Aerobic and anaerobic biodegradation of organics in the laboratory and the field have been modeled by first-order [1,4–12], zero-order [1,13], mixed-order [13,14] kinetics, Monod kinetics [15–20], and Michaelis–Menten Kinetics [4,21]. Haldane kinetics were used by Brown et al. [22] and Oh et al. [23]. The Monod kinetics used by Lodaya et al. [20] is a non-growth associated Michaelis Menten model since they ignored bacterial growth and decay.

Van Genuchten [24], van Genuchten and Alves [25], and Parker and van Genuchten [26] published a number of reports giving analytical solutions of the one dimensional advection dispersion equation supporting adsorption and first-order and/or zero-order production and decay for a number of initial and boundary conditions. The analytical solutions are based on constant pore water velocity and constant initial media concentration. In many experimental conditions, it is very difficult to maintain a constant velocity. Substantial permeability changes due to microbial growth [27,28] and gas production [29] have been reported. Solute transport modeling with time-dependent parameters is still in its infancy. Barry and Sposito [30] described a procedure to compute the analytical solution of the advection dispersion equation with time dependent transport parameters in case of nonreactive solutes only.

Solution of the one dimensional advection dispersion equation involving Monod and other kinetics involving microbial growth and decay is lacking in the literature. This article presents methods of solving the one-dimensional advection-dispersion equation with a variety of growth and non-growth associated kinetics including Monod kinetics. The pore water velocity has been taken as time-dependent and the initial porous media concentration has been taken as spatially variable. A number of initial and boundary condition has been considered to cover most possible cases of biodegradation studies in the laboratory and in the field. The first-order/zero-order model has been solved with the finite difference and orthogonal collocation method. Other models have been solved with the method of orthogonal collocation only. The models have been used to simulate one dimensional transport of BTX compounds with sorption and biodegradation given by several forms of treatment of the biodegradation kinetics.

2. Experimental setup

The experimental setup consists of a big sealed tank with dimensions of 800 cm × 30 cm × 30 cm filled with sand and acclimated microorganisms capable of biodegrading BTX compounds. The sand tank was used to simulate steady one-dimensional flow coupled with BTX transport through saturated sandy soil. Sampling ports are located at every 100 cm along the center of the tank. Liquid samples were taken at different times from the center of the sand tank using these sampling ports and analyzed by the flame

ionization detector (FID) of the gas chromatograph (GC). The concentration data thus collected at difference distances and times were fitted to the transport equations to compute the kinetics coefficients.

A $3(2^2)$ factorial design has been used to study the three factors on biodegradation rate of BTX compounds: groundwater velocity (1, 2, and 4 m/day), BTX concentration (10 ppm each and 50 ppm each) and dissolved oxygen (O:BTX = 1.5 and 3.2). A total bacteria plate count was conducted at the end of every run to monitor the growth and activity of the microorganisms in the sand tank. Soil samples were collected from five different locations along the length of sand tank. The total count of the mixed species ranged between 10^7 to 10^9 . A detailed description of the experimental work may be found in [31].

3. Governing equations

3.1. Transport equations

One dimensional advection–dispersion equation allowing sorption and first and/or zero order biodegradation is given by [26]:

$$D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} + \mu C + \gamma = R \frac{\partial C}{\partial t} \quad (1)$$

where C is the concentration of the solute in the liquid phase, D is the dispersion coefficient, v is the seepage or average pore water velocity in the x direction, μ is the overall first-order rate constant in the liquid and solid phase of the soil, and γ is the overall zero-order rate constant in the liquid and solid phase of the soil and R is the dimensionless retardation factor defined as

$$R = 1 + \rho k_d / \theta \quad (2)$$

where ρ is the porous medium bulk density; θ is the volumetric water content and k_d is the constant in the linear isotherm of the form

$$S = k_d C$$

S is the adsorbed concentration per unit mass of the solid phase.

The hydrodynamic dispersion coefficient D is expressed as [32]

$$D = \alpha v + D_m$$

where α is the coefficient of dispersivity and D_m is the coefficient of molecular diffusion which is very small compared to the hydrodynamic dispersion. Neglecting the molecular diffusion and taking v as a function of time, Eq. (1) can be written as

$$R \frac{\partial C}{\partial t} = \alpha v(t) \frac{\partial^2 C}{\partial x^2} - v(t) \frac{\partial C}{\partial x} + \mu C + \gamma \quad (3)$$

The transport equation for Monod kinetics can be written as

$$R \frac{\partial C}{\partial t} = \alpha v(t) \frac{\partial^2 C}{\partial x^2} - v(t) \frac{\partial C}{\partial x} + \frac{kXC}{K_s + C} \quad (4)$$

where

$$\frac{dX}{dt} = \frac{YkXC}{K_s + C} - bX \quad (5)$$

where X is the microbial concentration (total cell mass attached to the solid phase and suspended with liquid phase per unit volume of liquid phase, mg/L), k is the maximum specific substrate utilization rate (mg-substrate/mg-cells/day), K_s is the half saturation coefficient (mg-substrate/L), Y is the yield coefficient (mg cells produced/mg substrate consumed), b is the coefficient of overall biomass loss (per day) due to shear and decay.

For the nongrowth Michaelis Menten kinetics, the transport equation becomes

$$R \frac{\partial C}{\partial t} = \alpha v(t) \frac{\partial^2 C}{\partial x^2} - v(t) \frac{\partial C}{\partial x} + \frac{k_m C}{K_s + C} \quad (6)$$

where k_m is the maximum substrate utilization rate (mg-substrate/day) and is equivalent to kX in the Monod system assuming a constant biomass (X).

3.2. Boundary conditions

The initial condition was of the form

$$C(x, 0) = f(x) \quad (7)$$

where $f(x)$ is either a constant or a function of x measured along the length of the medium. Depending on whether the measured concentration is flux-averaged or volume averaged [26], the boundary conditions that can be applied at the inlet boundary ($x = 0$) are given by

$$C(0, t) = g(t) \quad (8)$$

or

$$C - \frac{D}{v} \frac{\partial C}{\partial x} \Big|_{x=0} = g(t)$$

that can be written as

$$C - \alpha \frac{\partial C}{\partial x}(0, t) = g(t) \quad (9)$$

Where $g(t)$ is the concentration of the solute injected at the inlet boundary which is

either a constant or a function of time. For the outlet boundary, the following condition was applied [26].

$$\frac{\partial C}{\partial x}(L, t) = 0 \tag{10}$$

Where L is the length of the porous media that may represent a sand tank or a soil column.

4. Solution methods

4.1. Finite difference solution

Eq. (3) can be written in dimensionless form with respect to the length of the sand tank. Substituting $x = ZL$ such that Z varies from 0 to 1 while x varies from 0 to L , we have

$$\frac{\alpha v(t)}{L^2} \frac{\partial^2 C}{\partial Z^2} - \frac{v(t)}{L} \frac{\partial C}{\partial Z} + \mu C + \gamma = R \frac{\partial C}{\partial t} \tag{11}$$

The initial and boundary conditions (Eqs. (8)–(10)) for the dimensionless system can be written as

$$C(Z, 0) = f(Z) \tag{12}$$

$$C(0, t) = g(t) \tag{13}$$

$$C - \frac{\alpha}{L} \frac{\partial C}{\partial Z}(0, t) = g(t) \tag{14}$$

$$\frac{\partial C}{\partial Z}(1, t) = 0 \tag{15}$$

Let U_j^n is the finite difference solution of C at $Z = jh$ and $t = n\kappa$, where h and κ are the finite difference grid interval and time step respectively. The following finite difference scheme which is similar to Crank–Nicholson’s has been used to solve Eq. (11) subject to initial condition (12) and boundary conditions (13 or 14) and (15).

$$\begin{aligned} & \frac{R}{4\kappa} \left\{ (U_{j+1}^{n+1} - U_{j+1}^{n-1}) + (U_j^{n-1}) \right\} \\ &= \frac{\alpha v(t)}{2h^2 L^2} \left\{ (U_{j+1}^{n+1} - 2U_j^{n+1} + U_{j-1}^{n+1}) + (U_{j+1}^n - 2U_j^n + U_{j-1}^n) \right\} \\ & - \frac{v(t)}{4hL} \left\{ (U_{j+1}^{n+1} - U_{j-1}^{n+1}) + (U_{j+1}^n - U_{j-1}^n) \right\} + \frac{\mu}{2} \{U_j^n + U_j^{n+1}\} + \gamma \end{aligned}$$

which simplifies to

$$-aU_{j-1}^{n+1} + bU_j^{n+1} + cU_{j+1}^{n+1} = aU_{j-1}^n + dU_j^n + eU_{j+1}^n + f\{U_j^{n-1} + U_{j+1}^{n-1}\} + \gamma$$

4.2. Solution by orthogonal collocation

Solution of the Monod system (Eqs. (4) and (5)) is presented in this article. The solution of other kinetics excluding microbial growth is relatively simpler. Substituting $x = ZL$ and dividing by R , the system of equations for the Monod kinetics can be written as

$$\frac{\partial C}{\partial t} = \frac{\alpha v(t)}{L^2 R} \frac{\partial^2 C}{\partial Z^2} - \frac{v(t)}{LR} \frac{\partial C}{\partial Z} + \frac{kXC}{R(K_s + C)}$$

which can be written as

$$\frac{\partial C}{\partial t} = f_1(t) \frac{\partial^2 C}{\partial Z^2} - f_2(t) \frac{\partial C}{\partial Z} + \frac{kXC}{R(K_s + C)} \tag{16}$$

where

$$\frac{dX}{dt} = \frac{YkXC}{K_s + C} - bX$$

Let C be approximated by non-symmetric polynomials of the type

$$C(Z, t) = (1 - Z)C(0, t) + ZC(1, t) + Z(1 - Z) \sum_{i=1}^M a_i(t) P_{i-1}(Z)$$

where a_i are arbitrary coefficients and P_i are the non-symmetric polynomials defined by the condition

$$\int_0^1 w(Z) P_n(Z) P_m(Z) dZ = 0$$

$n = 0, 1, 2, \dots, m - 1$

$W(Z) = 1$ in the present study

Let

$M =$ Number of internal collocation points.

$M2 = M + 2 =$ Total number of points including boundaries where U is to be computed.

$M1 = M + 1$

Writing Eq. (16) in collocation form (using $\frac{\partial C_j}{\partial Z} = \sum_{i=1}^{M2} A_{j,i} C_i$ and $\frac{\partial^2 C_j}{\partial Z^2} = \sum_{i=1}^{M2} B_{j,i} C_i$) we have

$$\frac{dC_j}{dt} = f_1(t) \sum_{i=1}^{M2} B_{j,i} C_i - f_2(t) \sum_{i=1}^{M2} A_{j,i} C_i + \frac{kX_j C_j}{R(K_s + C_j)} \tag{17}$$

$$\frac{dX_j}{dt} = \frac{YkX_j C_j}{K_s + C_j} - bX_j \tag{18}$$

Eqs. (17) and (18) represents $(2 * M2)$ coupled ordinary differential equations (ODEs) for solving $M2$ values of C_j and X_j at every time step. One way to solve this system is

to solve all these values of unknowns simultaneously by any numerical method such as Gill's method. The method used in the present study is very simple, but has been found to be efficient and accurate for a large number of cases. The method consists of decoupling the coupled system of ODEs by partial substitution of C_j from the previous time step and using a simple numerical method such as Euler's method or the Runge Kutta method to integrate the decoupled ODEs. The solution of X_j can be obtained by integrating Eq. (18) analytically between two time steps substituting the known values of C_j from the previous time step as follows:

$$\int_{x_1}^{x_2} \frac{dX_j}{X_j} = \int_{t_1}^{t_2} \left\{ \frac{YkC_j}{K_s + C_j} - b \right\} dt$$

Substituting the known values of X_j and the known values of C_j from previous time step in the second and third terms of Eq. (17), $M2$ independent ODEs for solving $M2$ values of C_j can be obtained as follows:

$$\frac{dC_j}{dt} = F(C_j, t) \quad (19)$$

The solution of the transport equation with other growth associated kinetics, such as the Haldane kinetics [22,23], can be similarly obtained modifying Eqs. (17) and (18). The collocation matrices A and B can be generated by the procedures described by Finlayson [33]. The collocation points between $x = 0$ to 1 can be computed along with A and B matrices.

4.3. Incorporating the boundary conditions

The boundary solutions, C_1 and C_{M2} can be computed from the boundary conditions as follows. When the inlet boundary condition is given by (13).

$$C_1 = g(t) \quad (20)$$

At the outlet we have

$$A_{M2,1}C_1 + \sum_{i=2}^{M1} A_{M2,i}C_i + A_{M2,M2}C_{M2} = 0$$

or

$$C_{M2} = \frac{1}{A_{M2,M2}} \left[- \sum_{i=2}^{M1} A_{M2,i}C_i - A_{M2,1}g(t) \right] \quad (21)$$

Now using the values of C_1 and C_{M2} from Eqs. (20) and (21) respectively in Eq. (17) we have

$$\begin{aligned} \frac{dC_j}{dt} = & g(t)(f_1(t)B_{j,1} - f_2(t)A_{j,1}) + (f_1(t)B_{j,M2} - f_2(t)A_{j,M2}) \frac{1}{A_{M2,M2}} \\ & \times \left[- \sum_{i=2}^{M1} A_{M2,i}C_i - A_{M2,1}g(t) \right] + f_1(t) \sum_{i=2}^{M1} B_{j,i}C_i - f_2(t) \sum_{i=2}^{M1} A_{j,i}C_i \\ & + \frac{kX_jC_j}{R(K_s + C_j)} \end{aligned} \quad (22)$$

Now integrating Eq. (22) for different values of j we get the solution of C at internal collocation points. Using Eqs. (20) and (21) we get the solution at the boundaries. When the inlet boundary condition is given by (14), by similar analysis the following equations can be obtained

$$C_1 = \frac{1}{S_1} \left\{ -A_{M2,M2} \left(Sg(t) + \sum_{i=2}^{M1} A_{1,i} C_i \right) + A_{1,M2} \sum_{i=2}^{M1} A_{M2,i} C_i \right\} \quad (23)$$

$$C_{M2} = \frac{1}{S_1} \left\{ A_{M2,1} \left(Sg(t) + \sum_{i=2}^{M1} A_{1,i} C_i \right) - (A_{1,1} - S) \sum_{i=2}^{M1} A_{M2,i} C_i \right\} \quad (24)$$

$$\begin{aligned} \frac{dC_j}{dt} = \frac{1}{S_1} (f_1(t) B_{j,1} - f_2(t) A_{j,1}) & \left[-A_{M2,M2} \left(Sg(t) + \sum_{i=2}^{M1} A_{1,i} C_i \right) \right. \\ & \left. + A_{1,M2} \sum_{i=2}^{M1} A_{M2,i} C_i \right] + \frac{1}{S_1} (f_1(t) B_{j,M2} - f_2(t) A_{j,M2}) \\ & \times \left[A_{M2,1} \left(Sg(t) + \sum_{i=2}^{M1} A_{1,i} C_i \right) - (A_{1,1} - S) \sum_{i=2}^{M1} A_{M2,i} C_i \right] \\ & \times f_1(t) \sum_{i=2}^{M1} B_{j,i} C_i - f_2(t) \sum_{i=2}^{M1} A_{j,i} C_i + \frac{kX_j C_j}{R(K_s + C_j)} \end{aligned} \quad (25)$$

where

$$S = L/\alpha, \text{ and } S_1 = (A_{1,1} - S) A_{M2,M2} - A_{1,M2} A_{M2,1}$$

4.4. Correction for abiotic losses

Three control runs with varied concentration, velocity and dissolved oxygen were conducted with 2 mg/L mercuric chloride to assess the removal of the BTX compounds in the sand tank due to abiotic sources, namely volatilization, chemical oxidation and sorption. The BTX concentration (ppm each), pore water velocity (m/day) and O:BTX ratio in the three control runs were (10, 4, 1.5), (30, 2, 3.2) and (50, 1, 3.2) respectively. Theoretically, benzene and alkyl benzenes are chemically stable when reacting with an ordinary oxidizing agent, such as $KMnO_4$, H_2O_2 , CrO_3 and HNO_3 . Lu [34] performed a number of batch studies to conclude that BTX compounds are not oxidized by H_2O_2 at concentrations as high as 2000 mg/L. Therefore chemical oxidation has been ignored in this study.

Volatilization loss in the inlet mixing tank was accounted by measuring the input concentration (C_0) in the sand media about 1 cm away from the screen separating the

inlet tank and the sand tank. Volatilization loss in the sand media was estimated from the control runs assuming first order removal [20]. The gross first order removal by biodegradation and volatilization was corrected by subtracting from the first-order removal by volatilization as shown below.

$$R \frac{\partial C}{\partial t} = \alpha v(t) \frac{\partial^2 C}{\partial x^2} - v(t) \frac{\partial C}{\partial x} + (\mu_{\text{biodegradation}} + \mu_{\text{volatilization}})C + \gamma$$

The values of μ computed in the main design points gives the sum of first-order coefficient attributed to biodegradation and volatilization. If U_c represents the concentration measured in the control runs, then

$$R \frac{\partial U_c}{\partial t} = \alpha v(t) \frac{\partial^2 U_c}{\partial x^2} - v(t) \frac{\partial U_c}{\partial x} + (\mu_{\text{volatilization}})U_c + \gamma$$

Thus μ computed from the control runs is $\mu_{\text{volatilization}}$ in the above equation. The mean first order removal rate ranged from 0.028/day for xylene to 0.052/day for benzene. The first-order volatilization removal as well as the retardation factor for each of BTX compounds has been found to be statistically independent of velocity and input concentration and DO. The biodegradation removal in the main experimental runs has

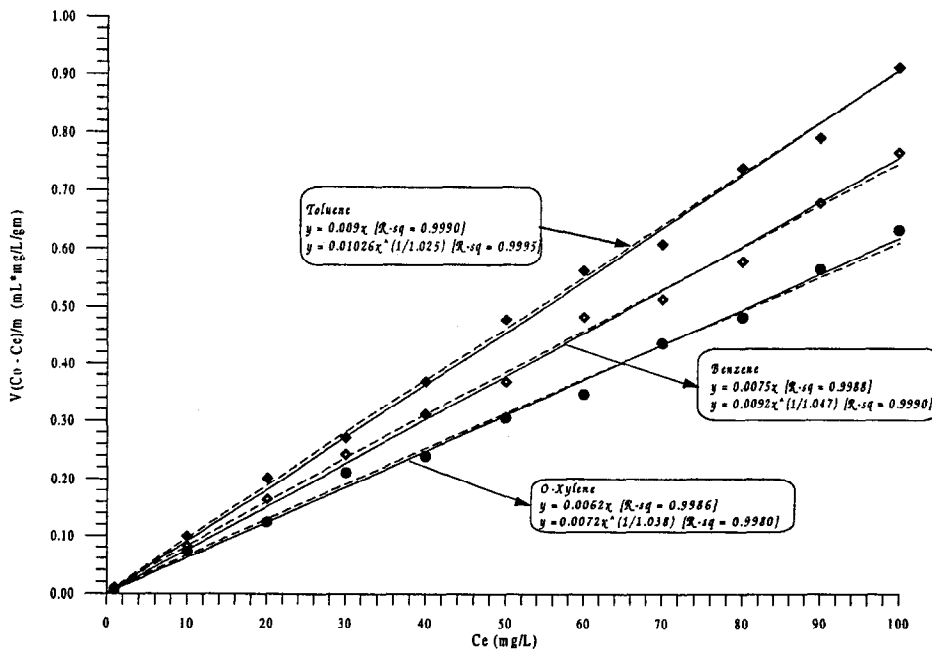


Fig. 1. Sorption isotherms (linear and Freundlich) of BTX compounds.

Table 1
Comparison of numerical solution with analytical solution for special cases

Boundary Condition →		C(0, t) = 10.00			$C - \frac{\alpha}{L} \frac{\partial C}{\partial Z}(0, t) = 10.00$		
T (days)	Distance (m)	Analytical	Finite diff.	Collocation	Analytical	Finite diff.	Collocation
2	0	10.0000	10.0000	10.0000	9.8636	9.8636	9.8593
2	1	8.1975	8.1976	8.2086	8.0842	8.0842	8.0956
2	2	6.6996	6.6960	6.6745	6.6053	6.6005	6.5858
2	3	5.4495	5.3934	5.4933	5.3680	5.3035	5.4122
2	4	4.2985	4.0610	4.2565	4.1972	3.9579	4.1561
2	5	2.7860	2.5792	2.7288	2.6303	2.4740	2.6145
2	6	1.1354	1.3130	1.1730	1.0317	1.2429	1.0881
2	7	0.4171	0.6198	0.3627	0.3971	0.5912	0.3428
2	8	0.3184	0.3832	0.3162	0.3173	0.3756	0.3221
4	0	10.0000	10.0000	10.0000	9.8636	9.8636	9.8731
4	1	8.1975	8.1976	8.1613	8.0842	8.0843	8.0583
4	2	6.6997	6.6998	6.7213	6.6054	6.6056	6.6371
4	3	5.4549	5.4551	5.4271	5.3766	5.3768	5.3546
4	4	4.4205	4.4207	4.4172	4.3554	4.3556	4.3540
4	5	3.5609	3.5608	3.5804	3.5068	3.5066	3.5265
4	6	2.8464	2.8440	2.8191	2.8015	2.7986	2.7741
4	7	2.2519	2.2368	2.2857	2.2142	2.1974	2.2482
4	8	1.7487	1.7158	1.7791	1.7149	1.6790	1.7462
6	0	10.0000	10.0000	10.0000	9.8636	9.8636	9.8712
6	1	8.1975	8.1976	8.1719	8.0842	8.0843	8.0651
6	2	6.6997	6.6998	6.7193	6.6054	6.6056	6.6301
6	3	5.4549	5.4551	5.4295	5.3766	5.3768	5.3558
6	4	4.4205	4.4207	4.4192	4.3554	4.3556	4.3580
6	5	3.5609	3.5611	3.5759	3.5068	3.5070	3.5252
6	6	2.8465	2.8467	2.8128	2.8015	2.8018	2.7719
6	7	2.2528	2.2530	2.2815	2.2155	2.2157	2.2473
6	8	1.7595	1.7748	1.7882	1.7285	1.7435	1.7594

been computed by subtracting the volatilization removal from the total first-order removal.

In the case of Monod kinetics, the transport equation has been modified as follows:

$$R \frac{\partial C}{\partial t} = \alpha v(t) \frac{\partial^2 C}{\partial x^2} - v(t) \frac{\partial C}{\partial x} + \frac{kXC}{K_s + C} - \mu_{\text{volatilization}} C$$

The retardation constant (*R*) was also computed from the control runs and additional batch tests. The batch tests were conducted following the procedure outlined in [35]. But no headspace was left in the samples and proper mixing was achieved using a rotary shaker. The sorption data was fitted to both linear and Freundlich isotherms (dotted lines) with high values of coefficient of determination (*R*²) as shown in Fig. 1. *C*₀ and *C*_∞ are the initial and equilibrium solution concentration (mg/L), *V* is the volume of

solution (mL), m is the mass (gm) of sand in a each tube on the shaker. According to the Freundlich isotherm, sorption at equilibrium is expressed by:

$$S = K_f C_e^{1/n}$$

where K_f is the sorption equilibrium constant and n is an empirical constant,. The value of R^2 was not improved in case of the Freundlich isotherm indicating that sorption of BTX compounds can be modeled assuming a linear isotherm in the transport equation. The values of n were also found to be close to 1. From the slope of the linear isotherms (k_d), the retardation factor (R) was computed using Eq. (2). The value of R for benzene, toluene, and o-xylene has been found to be 1.04, 1.05 and 1.03 respectively. These values are in good agreement with values of R computed by least squares fit of the three control runs data.

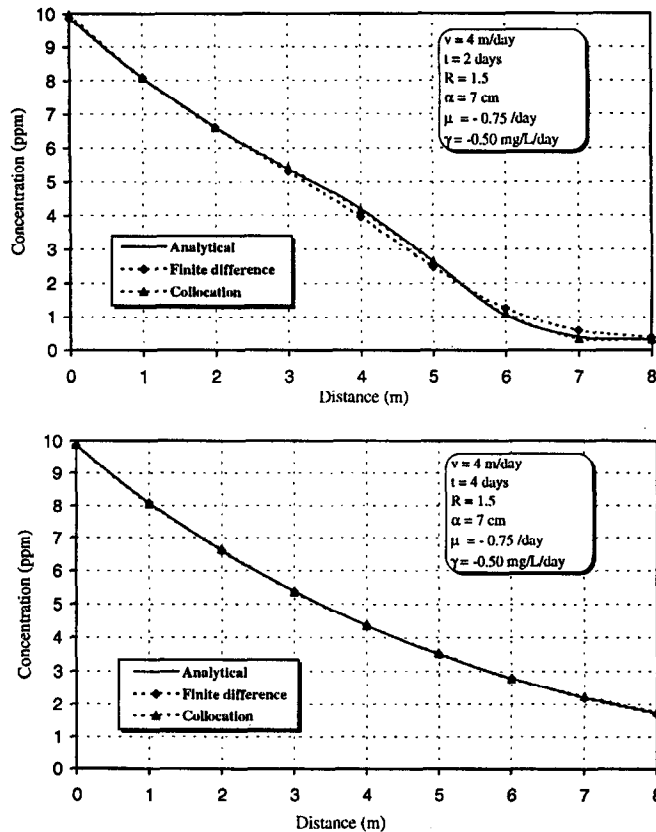


Fig. 2. Comparison of finite difference and orthogonal collocation solution for $t = 2$ days (top) and $t = 4$ days (bottom).

5. Parameter estimation

Parameters in the transport equations, such as α , R , μ , γ , k , k_m , K_s , Y , b were estimated by nonlinear least squares fit. Several methods of parameter estimation have been outlined by Parker and van Genuchten [26]. Least-square inversion methods have proved to be accurate and reliable tools for assessing parameters [26]. This method has found wide application for parameter estimation; some recent applications include [36–38].

A modified Gauss–Levenburg–Marquardt algorithm [39–41] has been used in the optimization technique. The initial estimation of the parameters were input from experience as the most probable values. A range for the values of each parameter was maintained during the convergence processes. An unmodified Gauss Newton method was adopted whenever possible. The unmodified Gauss method worked for cases where the number of parameters were three or less. Depending on the initial guess fast and accurate convergence was obtained; less than eight trials were needed in most cases.

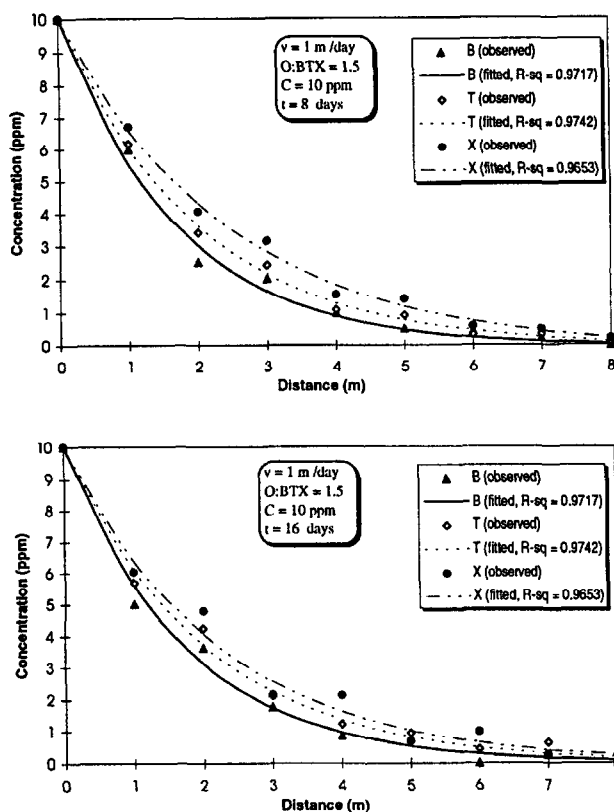


Fig. 3. Observed and fitted BTX concentration using the first order/zero order model for $t = 8$ days (top) and $t = 16$ days (bottom).

However in case of Monod kinetics, where the number of parameters is more, more trials were required.

6. Results

6.1. Comparison of finite difference and orthogonal collocation solution

The method of orthogonal collocation computes the solution only at the collocation points which are not necessarily the points where the solution with the finite difference method is obtained. For the sake of comparison, cubic spline interpolation was used to compute the solution of orthogonal collocation at the desired points. Both solutions have been found to be accurate compared with the analytical solution computed with CXTFIT [26]. The accuracy has been found to depend on the time step and grid interval or number of collocation points. However for the same computational time, the method of orthogonal collocation has been found to be more accurate especially at the unsteady

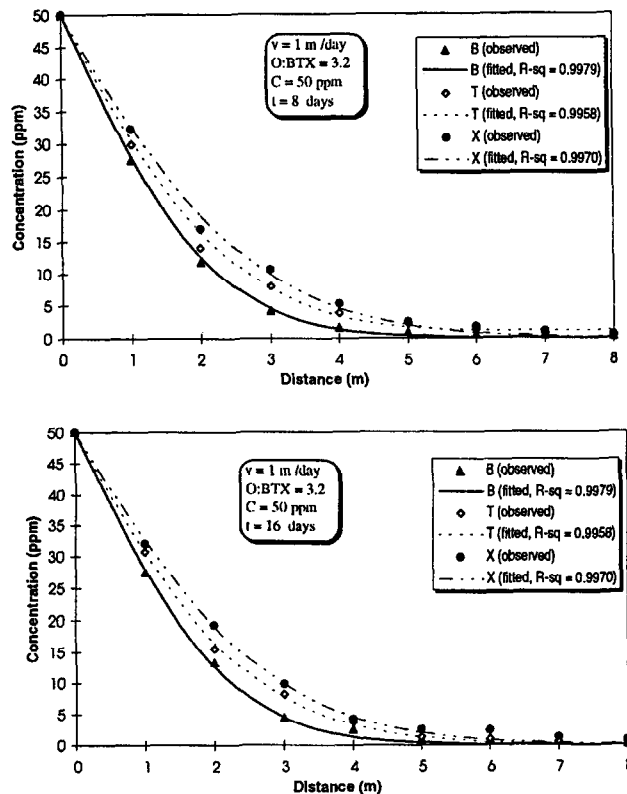


Fig. 4. Observed and fitted BTX concentration using the Michaelis Menten model for $t = 8$ days (top) and $t = 16$ days (bottom).

state. Table 1 shows numerical and analytical solutions for both the boundary conditions (13) and (14). Fig. 2 depicts the solutions for the boundary condition (14).

Different grid intervals ranging from 0.005 to 0.05 and time steps ranging from 0.02 days to 0.10 days have been tested for the finite difference method. A grid interval of 0.01 was found to be optimum. The solution for a time step of 0.02 days almost coincides with the analytical solution at steady state. The number of collocation points can be increased for higher accuracy. For the type of problems presented in this article, the optimum number of internal collocation points was found to be eight. More points did not improve the accuracy significantly but slowed down the solution. A time step of 0.02 days was found to be optimum for the orthogonal collocation method.

Solution of the Michaelis Menten model by the orthogonal collocation method has also been verified by setting $K_s = 0$ and comparing with the analytical solution of the zero-order model. Similarly solution of the Monod model has also been verified.

6.2. Evaluation of biodegradation kinetics

All models have been found to fit the experimental data with acceptable parameter values and acceptable R^2 (greater than 0.90). The first-order/zero-order model has been

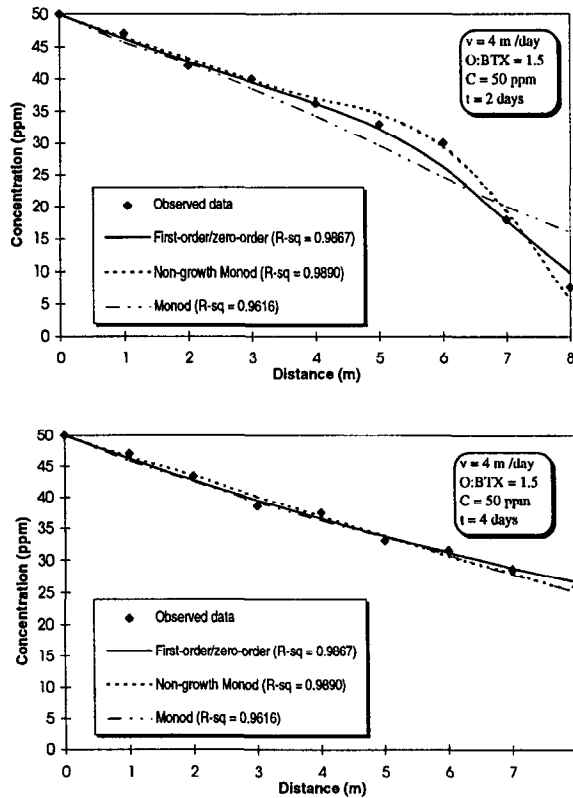


Fig. 5. Comparison of different models in simulating the observed benzene concentration for $t = 2$ days (top) and $t = 4$ days (bottom).

found to be adequate to describe the biodegradation process for the concentration range studied. The non-growth-associated Michaelis–Menten kinetics was found to equally describe the biodegradation process. However, the Monod kinetics including bacterial growth and decay has been found to be slightly inferior to the nongrowth Michaelis–Menten kinetics to fit the experimental data. The value of R^2 was slightly lowered in all cases. This might be due to fact that Monod kinetics allows bacterial growth as long as the substrate concentration is above the lower limit $\left(S_{\min} = \frac{bK_s}{Yk - b}\right)$; while in reality the growth of the microorganism reaches a steady state in the early stage of an experiment. Jones [21] found that substrate utilization might not necessarily be associated with bacterial growth and that a considerable proportion of substrate might be consumed without an equivalent increase in the microbial cell count. Alvarez et al. [15] observed that microbial count did not increase significantly from the initial count, prior to the addition of BTX compounds, to the time of biodegradation. They used a constant value of microbial mass (X) in the Monod model for prediction purposes. Lodaya et al. [20] also used Monod kinetics ignoring bacterial growth and decay.

Another reason for the poor fit to the Monod model is maintaining the biomass (X)

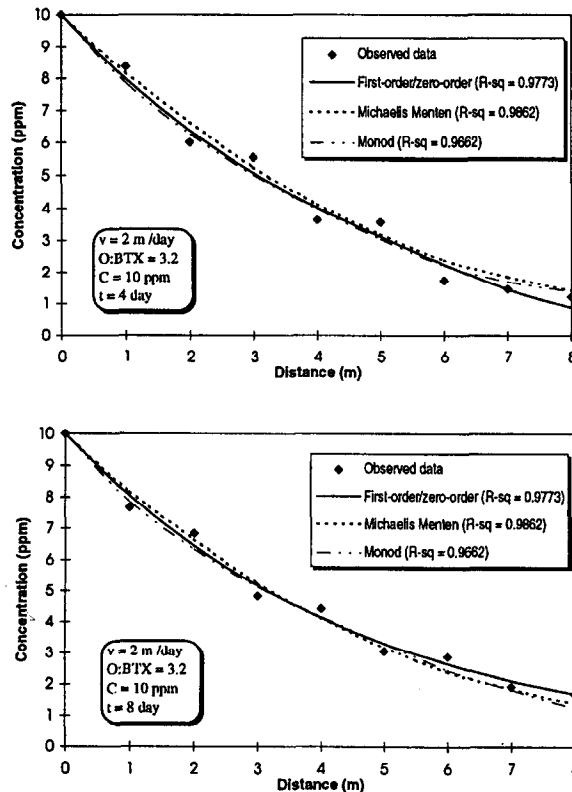


Fig. 6. Comparison of different models in simulating the observed toluene concentration for $t = 4$ days (top) and $t = 8$ days (bottom).

Table 2
Biokinetic constants for BTX biodegradation

References	k (mg/mg VSS-d)	K_s (mg/L)	Y (mg VSS/mg)	b (d ⁻¹)	k/K_s (L/mg-d)
BENZENE					
[42]	4.7	10.8	0.39	–	1.33
[18]	2.58	Small	0.65	0.11	–
[15]	8.3	12.2	0.0	0.0	0.65
[20]	3.3–7.5	3.3–40.0	0.0	0.0	–
This study, 1995	4.11–10.48	5.54–10.16	0.50–1.02	0.091–0.12	–
TOLUENE					
[43]	2.97	–	1.42	–	–
[44]	0.004–11.0	0.33–0.43	0.01–0.28	–	0.01–25.5
[45]	0.013–0.33	0.034–0.44	0.1	–	0.38–7.7
[46]	0.49	0.65	0.43	–	0.75
[47]	4.32	0.15	–	–	28.8
[15]	9.9	17.4	0.0	0.0	0.57
[18]	2.73	Small	0.66	0.11	–
This study, 1995	3.87–10.25	6.32–10.47	0.48–1.21	0.100–0.13	–
O–XYLENE					
[18]	3.03–3.18	0.1–0.8	0.67	0.11	3.8–30.0
This study, 1995	3.61–9.98	6.79–10.81	0.52–1.26	0.095–0.14	–

value measured at the beginning and end of each experimental run during the iteration process. A cell wet weight of 10^{-9} mg was assumed to convert cell numbers to biomass [15]. It has been found that the Monod kinetics with a constant value of X computed from the plate count at the end of each experimental run can be used to fit the data of that run. However, the fit was not found to be superior to the first-order and zero-order model in the case of low concentration of BTX compounds. Typical fitting of observed BTX data to the first order/zero order model is shown in Fig. 3. Typical fitting of observed BTX data to the Michaelis Menten model is shown in Fig. 4. Typical results of fitting the experimental data to all three models are shown in Figs. 5 and 6. The values of R^2 shown on all these figures are the combined coefficient of regression for fitting data plotted on the top and bottom of each figure.

The high value of R^2 for all the models were judged acceptable for fitting the observed BTX concentration data of this pilot study. The mean dispersivities computed from three control run were 7.02 cm for benzene, 6.47 cm for toluene and 6.11 cm for xylene. The values of kinetic coefficients, k_m , K_s and k for benzene, toluene, and xylene are shown in Table 2 which also shows values of those coefficients reported in the literature of a few other lab and field studies. Parameter values of this study are in between those reported for lab studies and those reported for field studies. In the case of a high concentration of BTX the values of K_s were increased to above 30 mg/L. R^2 was slightly lowered (1–3%) in the case of low concentration (10 mg/L of BTX each), but improved (1–3%) in case of high (50 mg/L). Thus the observed data in the case of

high concentration fitted better to the Michaelis Menten kinetics than to the first-order/zero-order model. Again in almost 90% of the cases (16 out of 18), the value of R^2 was higher than 0.95 for all regressions to first-order/zero-order or the Michaelis Menten model. Therefore the fits to first-order/zero-order model are good up to the range of the concentration of BTX compounds studied.

7. Conclusions

(a) A finite difference model has been developed for simulating one dimensional BTX transport allowing equilibrium sorption given by linear isotherm and biodegradation given by first-order and/or zero-order kinetics under a variety of initial and boundary conditions. The model considers time-dependent groundwater velocity and spatially variable initial concentration in addition to constant velocity and concentration. The model has been tested for high accuracy by comparing with the analytical solutions for special cases.

(b) An optimization routine has been developed using a modified Gauss Newton method to compute the transport parameters by nonlinear least squares fit to the above model. The least squares fitting procedure was found to converge rapidly regardless of the sign and magnitude of the initial guesses.

(c) A generalized model has been developed using orthogonal collocation for simulating one dimensional transport allowing equilibrium sorption given by linear isotherm and biodegradation given by a variety of biodegradation kinetics including or excluding microbial growth. Two models using Michaelis Menten and Monod Kinetics have been used for analysing the data collected in the present data. These models also consider time-dependent groundwater velocity and spatially variable initial concentration in addition to constant velocity and concentration and have been tested for accuracy.

(d) Models using Michaelis Menten and Monod kinetics have also been inverted using a modified Gauss–Levenberg–Marquardt's method. The objective was to study the suitability of these models, being frequently used in literature, to predict BTX fate in saturated sandy soil.

(e) Biodegradation of benzene, toluene and xylene in a mixture can be satisfactorily represented by first-order kinetics for the range of concentration studied (10 to 50 ppm each).

(f) Michaelis–Menten kinetics can be used to model BTX biodegradation in a mixture. Observed data corresponding to the input concentration of 50 mg/L has been found to fit better to this model than the first-order/zero-order model.

(g) Monod Kinetics with microbial growth and decay can also be used to model BTX biodegradation in a mixture. However with two more parameters (Y and b), the goodness of fit judged with the value of R^2 did not improve in the present study.

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