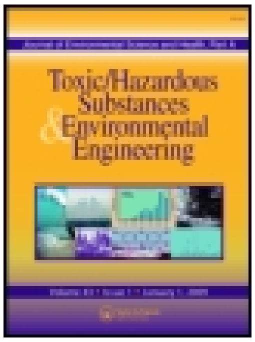

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Decay of Dissolved Substances by Second-Order Reaction. Problem Description and Batch-Reactor Solutions*

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ABSTRACT

The mass transport (advection-dispersion) equations allowing coupled second-order reaction (i.e. $\omega_1 C_1 + \omega_2 C_2 \xrightarrow{k_{12}} \text{Re}$) between two constituents are derived and result in a set of coupled nonlinear partial differential

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equations. Neglecting the spatial dependence simplifies the equations and produces coupled nonlinear ordinary differential equations for which several analytical solutions are provided. The solutions may be used to illustrate the effect of the second-order reaction mechanism as well as providing a means for evaluating the reaction constant k_{12}.

INTRODUCTION

In recent years, there has been great concern about the contamination of soils and aquifers with pollutants from agricultural, municipal and industrial activities. In agricultural areas, large amounts of pesticides have been applied to the soil, for example, 370,000 metric tons of active ingredients were used during 1982 in the USA (Cohen et al., 1984). Other areas of concern include nitrate contamination of the ground water due to cropping practices or from animal feedlots (U.S.G.S., 1985; Pye et al., 1983).

Organic pollutants have been shown to be contaminating the ground water by seepage from surface and underground storage tanks, evaporation ponds and lagoons (Pye et al., 1983; U.S.EPA., 1985; Panel on Groundwater Contamination, 1984). Several field investigations have been conducted to describe chemical migration from accidental or planned releases. McCarty et al. (1981) studied the movement of organics from a ground-water injection well. Hutchings et al. (1984) and Bedient et al. (1983) studied the movement of organics at rapid infiltration land treatment waste water treatment systems. Borden et al. (1986), Borden et al. (1984) and Bedient et al. (1984) have studied ground-water contamination from a wood creosoting site at Conroe, Texas.

At one time the presence and activity of microorganisms in aquifers was believed to be either limited or even non-existent. Some studies indicate that subsurface conditions do not preclude the existence of an active micro- flora and that bacteria could be found at extensive depths in the subsurface along with varying amounts of organic carbon (Dunlap and McNabb, 1973). In addition to natural microorganisms, other potential micropollutants include enteric microbial agents such as virus and bacteria (Bitton and Gerba, 1984; Gerba and Bitton, 1984), and protozoans (Craun, 1979, 1985; Beloin et al., 1986). Also, contamination of the ground water may occur from radioactive substances from temporary or long-term storage facilities (OTA, 1984; Pye et al., 1983; Panel on Groundwater Contamination, 1984).

Currently, half of the U.S.'s population uses ground water as their source of drinking water and in rural areas ground water comprises about 80 % of the drinking water needs (OTA, 1984). In Europe, 65 to 98 % of the population's drinking water comes from ground water (Milde et al., 1983). In many areas of the country, ground water is the sole source of potable water (Lehr et al., 1984). Thus, much emphasis has been place on pro- tecting the ground water supply from contamination.

Whether or not an aquifer becomes contaminated depends on many interrelated factors. Some of these factors include the hydrogeologic setting, climate, pollutant characteristics, microbiological environment, and decay phenomena. Equally important are preventative measures taken to en- sure that a pollutant remains contained in a storage or waste disposal site.

Once an aquifer is contaminated many of these same factors affect how long the contaminant will be present in the ground water as well as the overall areal extent affected by the pollutant. To date, there have been many investigations concerned with studying the persistence of pollutants in ground water. The persistence of microbial agents in ground water has been studied by Keswick et al. (1982) and Bitton et al. (1983), while Yates et al. (1985) studied the temperature effects on virus inactivation. Research concerned with the transformation of organic pollutants has been undertaken by Alexander (1980), Kobayashi and Rittmann (1982), Mackay et al. (1985), Macalady (1986), and Delfino and Miles

(1985) to mention a few. Recent efforts to model the transformation process are described by Borden and Bedient (1986) and Borden et al. (1986) who studied the biodegradation of hydrocarbons by bacteria.

Described in this paper are the equations that govern the transport and transformation of two reactive chemical constituents in ground water where the influences of inter-constituent reaction is allowed. Several exact solutions to the coupled nonlinear equations for a stagnant flow system are provided which illustrate the second-order decay mechanism. Although the assumptions applied in developing these solutions limit their usefulness in modeling the contaminant transport process in flow fields, they do provide a means for verifying more comprehensive finite-difference or finite-element solutions to the governing equations and, more importantly, provide a means whereby the reaction coefficients for batch reactor experiments may be obtained.

THE TRANSPORT EQUATIONS

Consider a homogeneous isotropic incompressible porous medium which contains in aqueous solution a chemical substance, denoted as C_{1a}, where the substript "1" denotes chemical 1. Further, assume that another chemical substance is present (denoted C_{2a}) which reacts with C_{1a} according to the second-order reaction mechanism (Ames, 1965; Smith, 1956)

$$\omega_1 C_{1a} + \omega_2 C_{2a} \xrightarrow{k_{12}} \mathrm{Re} \qquad (1)$$

where ω_1 and ω_2 are the stochiometric coefficients, k_{12} is the rate constant for the reaction and Re are the products of the reaction. In the following discussion, it is assumed that the reaction given by Eq. 1 is irreversible.

For simplicity, the analytical solutions derived herein assume the condition $\omega_1 = \omega_2 = 1.0$. To obtain the solution when $\omega_1 \neq \omega_2$ it is only necessary to alter the coefficients of the governing equation. Since the ω_i's are constants, they can be grouped with the coefficients: R_i, D_i, V_i, k_i and k_{12} (discussed below) to give new coefficients: $\underline{R}_i = \omega_i R_i$, $\underline{D}_i = \omega_i D_i$, $\underline{V}_i = \omega_i V_i$, $\underline{k}_i = \omega_i k_i$ and $\underline{k}_{12} = \omega_1 \omega_2 k_{12}$. These new coefficients are then used in the solutions for C_{1a} and C_{2a} given below.

The approach to describe the chemical transport process used here is similar to that of Enfield et al. (1986). The compounds of interest are assumed to be miscible in the liquid phase and non-volatile. Although these assumptions will be used here, fluids with an immiscible phase may also be treated (see Enfield, 1985). A solute may react with the solid phase by sorption, be transformed while sorbed or transported and/or transformed in the liquid phase. A vapor phase may be present but is assumed not to participate in the transport or transformation processes.

Mathematically, the transport process is described by equating various fluxes through an elemental volume and adding any sink mechanisms. A non-zero quantity represents a change in storage. Following the notation of Enfield (1985), the transport process in the aqueous phase can be written as

$$\frac{\partial(\theta\rho_a C_{ia})}{\partial t} - D_{ia}\frac{\partial^2(\theta\rho_a C_{ia})}{\partial x^2} + V_{ia}\frac{\partial(\theta\rho_a C_{ia})}{\partial x} = - k_{ias}(\theta\rho_a C_{ia}) + k_{isa}(\rho_b)C_{is} - k_{ita}(\theta\rho_a C_{ia}) - \bar{k}_{12}(\theta\rho_a)^2 C_{1a}C_{2a} \qquad i = 1,2 \tag{2}$$

where each symbol in Eq. 2 is described in the Appendix.

Each term in Eq. 2 describes a different part of the transport process. In particular, the three terms on the left-hand side of Eq. 2 describe the time rate of change in mass, the dispersion-diffusion process and advection, respectively. The right-hand side of Eq. 2 describes the effect of various source/sink terms such as the sorption and transformation processes. The last term of Eq. 2 describes the coupled transformation of component "1" in the presence of "2" by the second-order reaction mechanism.

The concentrations on the solid phase are given by an equation similar to Eq. 2 except that the dispersion and advection processes are not included. This is a good assumption since the soil matrix is stationary.

$$\frac{\partial(\rho_b C_{is})}{\partial t} = -k_{isa}(\rho_b)C_{is} + k_{ias}(\theta\rho_a)C_{ia} - k_{its}(\rho_b)C_{is} \qquad i=1,2 \tag{3}$$

The mathematical model developed herein assumes that the reaction between the two chemical components described by Eq. 1 can occur only in the aqueous phase. If the chemicals can react in the solid phase as well, an additional term is subtracted (i.e. $\bar{k}_{12}(\theta\rho_b)^2 C_{1s}C_{2s}$) from the right-hand side of Eq. 3.

The total change in mass in the elemental volume is found by adding Eq. 2 to Eq. 3. That is,

$$\begin{aligned}\frac{\partial(\theta\rho_a C_{ia})}{\partial t} + \frac{\partial(\rho_b C_{is})}{\partial t} - D_{ia}\frac{\partial^2(\theta\rho_a C_{ia})}{\partial x^2} + V_{ia}\frac{\partial(\theta\rho_a C_{ia})}{\partial x} \\ = -k_{ita}(\theta\rho_a C_{ia}) - k_{its}(\rho_b)C_{is} - \bar{k}_{12}(\theta\rho_a)^2 C_{1a}C_{2a} \\ i=1,2\end{aligned} \tag{4}$$

Eq. 4 is written with two unknowns: the concentration of each component in the aqueous phase (C_{ia}) and on the solid phase (C_{is}). To write Eq. 4 in terms of the aqueous phase, a relationship describing the transfer between the aqueous and solid phases is needed. The rate, r_i, in which the sorption process occurs can be written as

$$r_i = k_{ias}(\theta\rho_a)C_{ia} - k_{isa}\rho_b C_{is} \tag{5}$$

Many studies have shown that equilibrium for the reaction in Eq. 5 takes place rapidly and is approximately reversible (e.g. Schwartzenbach and Westall, 1981). For such situations the net rate of change from one phase to the other is zero and the mass ratio would be the equilibrium constant

$$\frac{C_{is}}{C_{ia}} = \frac{k_{ias}(\theta\rho_a)}{k_{isa}\rho_b} = k_{id} \tag{6}$$

where k_{id} is a unitless linear sorption partition coefficient. Defining $k'_{id} = k_{ias}/k_{isa}$ and if local equilibrium exists, Eq. 4 can be rewritten in terms of one dependent variable

$$R_i \frac{\partial C_{ia}}{\partial t} = D_{ia} \frac{\partial^2 C_{ia}}{\partial x^2} - V_i \frac{\partial C_{ia}}{\partial x} - k_i C_{ia} - \underset{i=1,2}{k_{12} C_{1a} C_{2a}} \tag{7}$$

where R_i is the retardation factor for component "i" (i.e. $R_i = 1 + k'_{id}$), k_i is the lumped transformation coefficient $k_i = k_{ita} + k'_{id}k_{its}$ and $k_{12} = \bar{k}_{12}(\theta\rho_a)$. If second-order reaction occurs on the solid phase then $k_{12} = \bar{k}_{12}(\theta\rho_a)[1 + k'_{1d}k'_{2d}]$.

Eq. 7 is a coupled nonlinear partial differential equation where the "product nonlinearity" as well as the coupling are due to the right-most term of Eq. 7.

MEAN FLUID VELOCITY

Each chemical constituent in Eq. 7 is allowed to have a different average interstitial velocity. At first, this may seem inappropriate but there is growing evidence that some compounds such as macromolecules (Enfield and Bengtsson, 1987, in review) and microorganisms (Wollum and Cassel, 1978; Gronden and Gerba, 1986) that, when excluded from the smaller soil pores, have average pore water velocities that are different than other compounds or solutes; thus this condition may be necessary. The typical case where $V_1 = V_2 =$ constant is still provided by the equation and solutions contained herein and only causes an additional restriction on the coefficients. Also, since ω_1 may not be the same as ω_2 the adjusted values $\underline{V}_1$ and $\underline{V}_2$ may not be the same even when $V_1 = V_2$.

TRANSFORMED VARIABLE

If it is assumed that the properties of each chemical are such that the following relationship holds

$$\epsilon = \frac{R_2}{R_1} = \frac{D_2}{D_1} = \frac{V_2}{V_1} = \frac{k_2}{k_1} \tag{8}$$

where the subscript "a" has been dropped since we are only concerned with the aqueous phase. A new dependent variable, $C^*(x,t)$,

$$C^*(x,t) = C_1(x,t) - \epsilon C_2(x,t) \tag{9}$$

can be defined which will enable Eq. 7 to be written with the same form as the advection-dispersion equation, that is,

$$R_1 \frac{\partial C^*}{\partial t} = D_1 \frac{\partial^2 C^*}{\partial x^2} - V_1 \frac{\partial C^*}{\partial x} - k_1 C^* \tag{10}$$

Given appropriate initial and boundary conditions for $C^*(x,t)$, solutions to Eq. 10 can be readily obtained (see van Genuchten and Alves, 1982).

The solution to Eq. 10 may be useful in providing a means for determining k_{12} (Ames, 1965) given specific conditions on the coefficients in Eq. 10 but, in general, the solution to Eq. 10 does not readily provide a means for obtaining C_1 and C_2, unless another relationship between C_1 and C_2 is known.

ANALYTICAL SOLUTIONS FOR BATCH REACTORS SYSTEMS

Although, in general, Eq. 7 is not amenable to analytic solution, if the x-dependence is removed several simple solutions may be obtained. For a batch-reactor system, $D_i = V_i = 0$. Under these conditions Eq. 7 can be written as

$$R_1 \frac{dC_1}{dt} = - k_1C_1 - k_{12}C_1C_2 \tag{11a}$$

$$R_2 \frac{dC_2}{dt} = - k_2C_2 - k_{12}C_1C_2 \tag{11b}$$

CASE I: No first-order decay (i.e. $k_1 = k_2 = 0$)

For this situation subtracting Eq. 11a from Eq. 11b eliminates the nonlinear terms and a new dependent variable is produced

$$\frac{dC^*}{dt} = 0 \tag{12}$$

where $C^*(t) = R_1C_1(t) - R_2C_2(t)$. The solution to Eq. 12 is a constant and given the initial condition, $C^*(0) = R_1C_1(0) - R_2C_2(0)$ a relationship between $C_1(t)$ and $C_2(t)$ can be found. That is,

$$C^*(t) = R_1C_1(t) - R_2C_2(t) = C^*(0) \tag{13}$$

Incorporating $C_2(t)$ from Eq. 13 into Eq. 11a and rearranging gives a nonlinear ordinary differential equation in one dependent variable

$$\frac{dC_1}{dt} + \epsilon_2 C_1^2 + aC_1 = 0 \tag{14}$$

where $\epsilon_2 = k_{12}/R_2$ and $a = k_{12}C^*(0)/R_1R_2$ and has the solution (see Kamke, 1943, esp. p. 298)

$$C_1(t) = \frac{C_1(0)}{e^{-at} + R_1C_1(0)[1 - e^{-at}]/C^*(0)}; \quad (C^*(0) \neq 0) \tag{15}$$

The concentration of $C_2(t)$ can be found by using Eq. 13. If it is further assumed that $R = R_1 = R_2$ and that $C_o = C_1(0) = C_2(0)$, then $C(t) = C_1(t) = C_2(t)$ and the solution for the aqueous concentration for both constituents is

$$C(t) = \frac{C_o}{1 + k_{12}C_ot/R} \tag{16}$$

which is the standard solution for a second-order rate equation (see Smith, 1965).

CASE II: First-order Decay of Both Components and $\epsilon = R_2/R_1 = k_2/k_1$.

For this case, subtracting equation Eq. 11a from Eq. 11b and solving the ordinary differential equation for $C^*(t)$ gives

$$C^*(t) = C_1(t) - \epsilon C_2(t) = C^*(0)\exp(-k_1t/R_1) \tag{17}$$

Solving for $C_2(t)$ from Eq. 17 and incorporating it into Eq. 11a and rearranging gives the nonlinear ordinary differential equation for $C_1(t)$ analogous to Eq. 14 where $\epsilon_2 = k_{12}/R_2$ and $a(t) = [k_1/R_1 - k_{12}C^*(t)/R_2]$. The solution is again found from Kamke (1943)

$$C_1(t) = \frac{C_{1o}}{(1-C_{1o}/C_o^*)\exp\{\lambda t + (b/\lambda)[\exp(-\lambda t)-1]\} + C_{1o}\exp(-\lambda t)/C_o^*} \tag{18}$$

where $\lambda = k_1/R_1$, $b = \epsilon_2C_o^*$, $C_{1o} = C_1(0)$ and $C_o^* = C^*(0) \neq 0$. The concentration of $C_2(t)$ in the aqueous solution can be found by using Eq. 17. If $\epsilon = 1$ and $C_1(0) = C_2(0)$ then $C_1(t) = C_2(t)$. Under these conditions the solution to Eq. 11a is

$$C_1(t) = \frac{C_{1o}}{\exp(\lambda t) + C_{1o}k_{12}[\exp(\lambda t)-1]/k_1} \tag{19}$$

CASE III: First-order Decay of One Specie (i.e. $k_2 = 0$ and $k_1 \neq 0$).

For this situation a new variable like $C^*(t)$ cannot be defined. The solution for this problem is found by direct integration of Eq. 11 and using a transform relationship. Since an analytical solution to the second integral for the transform relationship with respect to time was not found, the solution is given in implicit form.

In the following discussion, it is assumed that C_2 doesn't undergo first-order decay. Integrating Eq. 11b directly subject to the initial condition $C_2(0) = C_{2o}$ gives

$$C_2(t) = C_{2o}\exp\left[-(k_{12}/R_2)\int_o^t C_1(t)dt\right] \tag{20}$$

Incorporating Eq. 20 into Eq. 11a gives

$$\frac{dC_1}{dt} = -\lambda_1 C_1 - \epsilon_1 C_1 C_{2o}\exp\left[-\epsilon_2\int_o^t C_1(t)dt\right] \tag{21}$$

Defining the transform relationship $\psi(t) = \epsilon_2\int_o^t C_1(t)dt$ allows Eq. 21 to be rewritten as

$$\frac{d^2\psi}{dt^2} = -\lambda_1\frac{d\psi}{dt} - b\frac{d\psi}{dt}\exp(-\psi) \tag{22}$$

where $b = \epsilon_1 C_{2o}$. Eq. 22 can be directly integrated by noting that $\exp(-\psi)d\psi/dt = -d\exp(-\psi)/dt$. Carrying out this integration and incorporating the boundary conditions $\psi(0) = 0$ and $d\psi/dt|_{t=0} = \epsilon_2 C_1(0) = \epsilon_2 C_{1o}$ gives

$$\frac{d\psi}{dt} = -\lambda_1\psi + b[\exp(-\psi) - 1] + \epsilon_2 C_{1o} = \epsilon_2 C_1(t) \qquad (23)$$

Since $C_1(t)$ may not be negative, the restriction, $\psi < \psi_{max}$, is adopted where ψ_{max} is the value of ψ when $C_1(t)$ first becomes zero and occurs at time, t_{max}.

To obtain an explicit relationship between C_1 (also C_2) with respect to time, it is necessary to integrate Eq. 23 with respect to time, solve for ψ explicitly and then differentiate to obtain an expression for $C_1(t)$ that is explicit in time. Since no analytical solution to Eq. 23 was found, an implicit method for solving for $C_1(t)$ and $C_2(t)$ is necessary. The first step in the implicit solution is to choose a value of ψ which allows one to obtain an exact value of the concentration C_1 [also $C_2(t)$ since $C_2(t) = C_{2o}\exp(-\psi)$] from Eq. 23. Since the time is not specified when using Eq. 23 it must be found by numerically integrating Eq. 23 as follows

$$\int_o^{\psi<\psi_{max}} \frac{d\psi}{-\lambda_1\psi + b[\exp(-\psi) - 1] + \epsilon_2 C_{1o}} = \int_o^{t<t_{max}} dt \qquad (24)$$

For $t > t_{max}$, $\psi = \psi_{max}$ and the concentration of $C_1(t>t_{max}) = 0$.

An approximate solution for t and $C_1(t)$ for small ψ's (and therefore small times) can be found by using the approximation for the exponential, $e^{-x} \simeq 1 - x + x^2/2$. Using this approximation in Eq. 24 and integrating gives (Dwight, 1961)

$$t = 2\Big[\ln[(\psi-p)/(\psi-q)] - \ln[p/q]\Big]/b(p-q)$$

$$C_1(t) = \frac{(p-q)(qp^2-pq^2)\exp[(p-q)bt/2]}{2\epsilon_2\{p\exp[(p-q)bt/2] - q\}^2} \qquad (25)$$

where p and q are the roots to the quadratic equation; $b\psi^2/2 + (-\lambda_1-b)\psi + \epsilon_2 C_{1o}$ and $\Delta = 2b\epsilon_2 C_{1o} - (b+\lambda_1)^2 < 0$. For $\Delta > 0$ the approximate solution to Eq. 24 is

$$\begin{aligned} t &= 2\left[\tan^{-1}[(b\psi-b-\lambda_1)/\sqrt{\Delta}] + \tan^{-1}[(b+\lambda_1)/\sqrt{\Delta}]\right]/\sqrt{\Delta} \\ C_1(t) &= \Delta\sec^2\left[\sqrt{\Delta}\,t/2 - \tan^{-1}[(b+\lambda_1)/\sqrt{\Delta}]\right]/2b\epsilon_2 \end{aligned} \tag{26}$$

and for $\Delta = 0$

$$\begin{aligned} -t &= \frac{2}{b(\psi-1) - \lambda_1} + \frac{2}{b + \lambda_1} \\ C_1(t) &= \frac{1}{2b\epsilon_2[t/2 + 1/(b+\lambda_1)]^2} \end{aligned} \tag{27}$$

In general, since the approximate time, t, is determined by an integration (as opposed to a differentiation), accurate results were obtained in the examples contained in Table 1 for values of ψ from about $0.4\psi_{max}$ to $0.95\psi_{max}$ (for the solid, dotted and dashed lines, respectively, ψ_{max} is 0.5671, 1.745 and 0.09487). The approximate concentrations $C_1(t)$ and $C_2(t)$, on the other hand, were found to be less accurate than t even for relatively low values of ψ. This is due in part to two factors: first the concentrations are based on an approximate relationship between ψ and t and second, they are derived from a differentiation. Therefore, any errors introduced by the approximation propagate more strongly through the differentiation process. Since exact values of $C_1(t)$ can be found from Eq. 23, there is no reason to use the approximate solutions for the concentrations. They are included, however, for completeness as they point to a means for obtaining exact values for $C_1(t)$ whenever the integral can be solved explicitly for ψ.

Table 1. Comparison between the analytical and approximate solution for Case III. The results for the solid, dotted and dashed lines are the same as in Fig. 3. The values for y_{max} for the solid, dotted and dashed lines are 0.5671, 1.745 and 0.09487, respectively.

Solid Line

T^*	C_1	C_2	ψ	T^*_{app}	C_{1app}
0.10	0.822	0.913	0.091	0.100	0.823
0.30	0.568	0.796	0.228	0.300	0.570
0.50	0.400	0.723	0.324	0.498	0.405
1.00	0.173	0.632	0.459	0.978	0.188
1.50	0.077	0.596	0.518	1.410	0.098
2.00	0.035	0.580	0.545	1.759	0.059
3.00	0.007	0.570	0.563	2.154	0.033
5.00	0.000	0.567	0.567	2.302	0.027

Dotted Line

T^*	C_1	C_2	ψ	T^*_{app}	C_{1app}
1.00	0.449	0.516	0.662	0.976	0.660
2.00	0.265	0.365	1.007	1.771	--†
3.00	0.173	0.295	1.221	2.310	--
4.00	0.119	0.255	1.365	2.657	--
5.00	0.084	0.231	1.465	2.883	--
6.00	0.061	0.215	1.537	3.035	--
8.00	0.033	0.196	1.629	3.213	--
10.00	0.019	0.187	1.679	3.305	--

Dashed Line

T^*	C_1	C_2	ψ	T^*_{app}	C_{1app}
0.50	0.583	0.962	0.039	0.500	0.583
1.00	0.345	0.941	0.061	1.000	0.345
1.50	0.206	0.928	0.075	1.499	0.206
2.00	0.123	0.921	0.083	1.996	0.124
2.50	0.074	0.916	0.088	2.491	0.075
3.00	0.045	0.914	0.090	2.981	0.046
5.00	0.006	0.910	0.094	4.809	0.007
10.00	0.000	0.909	0.095	6.428	0.001

† - indicates a value greater than 1.0

EXAMPLES

To illustrate the effect of chemical reaction on the transport process, several examples are described that use the analytical solutions given in cases I, II and III and a finite difference approximation to Eq. 7. For the finite difference approximation, it was assumed that diffusion-dispersion and advection were negligible. This simplifies the transport process and allows the effects due to the second-order reaction mechanism between the two chemical species to be demonstrated in a lucid manner.

Shown in Figure 1 are the concentration profiles with respect to the normalized time ($T^* = tk_{12}$) that result from using Eq. 15 and Eq. 16 (solid lines) and by the finite difference method (dots). The time scale has been normalized so that each unit represents a time of $1/k_{12}$ and for all the examples shown $k_{12} = 0.1$. If two chemicals are present and do not react with one another the time rate of change of each specie is given by the curve marked "no-reaction". This is a case where k_{12} in Eq. 11 is zero. Also shown in Figure 1 are the concentration profiles when second-order reaction is accounted for. For a situation where the retardation constants have an equal value (i.e. $R_1 = R_2$), the time rate of change in the concentration of either component is shown by the curve marked "$C_1 = C_2$". As shown in Figure 1, after $T^* = 10$ less than 10% of the original concentration of each chemical remains. This demonstrates how the second-order reaction mechanism can remove an undesired substance from a region provided that another harmless substance can be found and that this substance will react with the other and produce harmless by-products.

The effect of different retardation coefficients is also shown in Figure 1 where the dashed curve marked "C_1" has $R_1 = 1$ and the curve "C_2" has $R_2 = 10$. It is evident from this figure that the concentration profiles for the two species are no longer the same. This is due to the

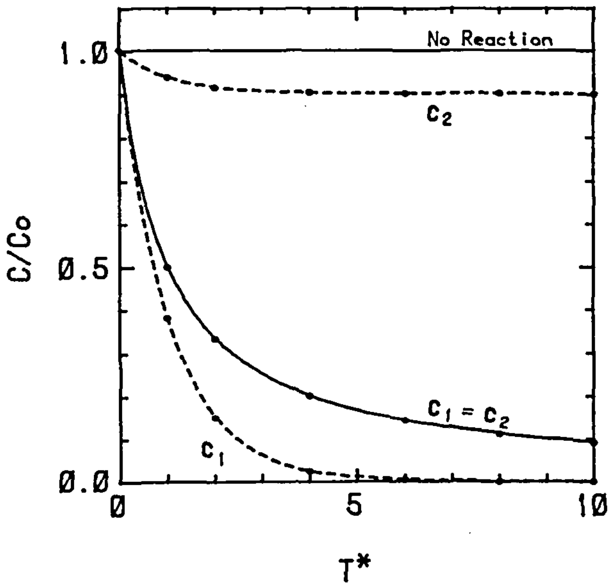

Fig. 1 Concentration profile with respect to normalized time, $T^* = K_{12}t$ for case I. The retardation coefficients are $R_1 = R_2 = 1$ for the no reaction and $C_1 = C_2$ cases. For the $C_1 \neq C_2$ profiles, $R_1 = 1$ and $R_2 = 10$. The dots indicate the concentrations obtained by finite-difference.

influx of specie "2" into the fluid phase from the adsorbed phase. The addition of C_2 from the solid phase causes the concentration of C_2 to be elevated compared to C_1. Assuming that C_2 is the undesired specie, only 10% of C_2 is removed via the second-order reaction mechanism. Although an equal quantity of each specie is removed from the system, some of the C_2 has desorbed from the soil to maintain equilibrium conditions. The limiting behavior can also be demonstrated analytically using Eq. 15. If $C^*(0)$ is less than zero, the limiting value for $C_1(t)$ is $C_{1o}-R_2C_{2o}/R_1$ and $C_2(t)$ is zero. If, as is the case for this example, $C^*(0)$ is greater than

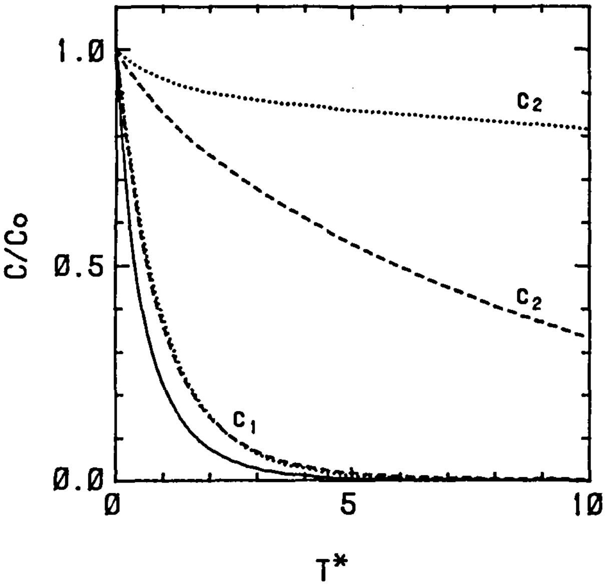

Fig. 2 Concentration profile with respect to normalized time, $T_* = k_{12}t$ for Case II. $R_1 = \epsilon = 1$ and $k_1 = k_2 = k_{12}$, for the solid line and $\epsilon = 10$, $R_1 = 1$, $\epsilon = 10$ and $k_1 = .01k_{12}$ for the dotted line and $R_1 = 1$, e = 10 and $k_1 = .1k_{12}$ for the dashed line.

zero, the limiting value for $C_1(t)$ is zero and $C_2(t)$ is C_{2o}-R_1C_{1o}/R_2. To reduce $C_2(t)$ to a low level, either repeated additions of $C_1(t)$ or a much higher initial concentration of C_1 (compared to C_2) would be necessary.

The second example, shown in Figure 2, gives the concentration profiles when first-order decay is included in the problem. The solid line is for a case where the first-order decay coefficient has the same magnitude as k_{12} and R_1=R_2 (i.e. ϵ=1). For this situation, the concentration profile for $C_1(t)$ and $C_2(t)$ are the same. For the cases illustrated here, this concentration profile decays the fastest because the first-order decay coefficient is the largest considered and neither specie adsorbs to the soil matrix.

The dotted lines indicates the concentration profile for each specie (marked on line) when $k_1 = 0.01k_{12}$, $R_1 = 1$ and $\epsilon = 10$ and the dashed line is for $k_1 = 0.1k_{12}$, $R_1 = 1$ and $\epsilon = 10$. Comparing the concentration profiles for the solid and dotted lines with Figure 1 shows the effect of the first-order decay coefficient. When decay is included into the problem, the concentration for both components approaches zero at large times. For the examples shown in Figure 2, when $R_1 \neq R_2$ the second-order reaction mechanism appears to operate over relatively short time periods relative to the species with the larger retardation coefficient. In Figure 2, after a T^* of about 2, the second-order reaction mechanism is no longer affecting the concentration of C_2 and first-order decay is the primary cause for the reduction in C_2. Another way to view this is that as either component approaches zero the second-order term in Eq. 11 approaches zero due to the effect of the multiplication.

Shown in Figure 3 are the concentration profiles for a two chemical system using the third solution (Eqs. 23 and 24). For the solid and dotted lines, the retardation coefficients for both components are equal to unity (i.e. no sorption). For the dashed lines, $R_1 = 1$ and $R_2 = 10$. The first- order decay coefficient for C_1 (recall that $k_2 = 0$) was equal to k_{12} for the solid line and $k_1 = 0.1k_{12}$ for the dotted and dashed lines. The dots on the solid line are from the finite difference solution and are used as one means for verifying the solution given by Eq. 24.

Several observations can be made concerning the concentration profiles in Figure 3. First, as $k_1 \rightarrow 0$ the profiles for $C_1(t)$ approach $C_2(t)$ (i.e. compare solid with the dotted lines). Also, as is the case for all the solutions presented here, when the retardation coefficients are not equal the chemical components with the larger retardation coefficient has higher concentration at any time compared to the other. Since the concentration of the highly retarded chemical remains elevated (compared to the $R_1 = R_2$ case, i.e. dotted and dashed lines), the profile

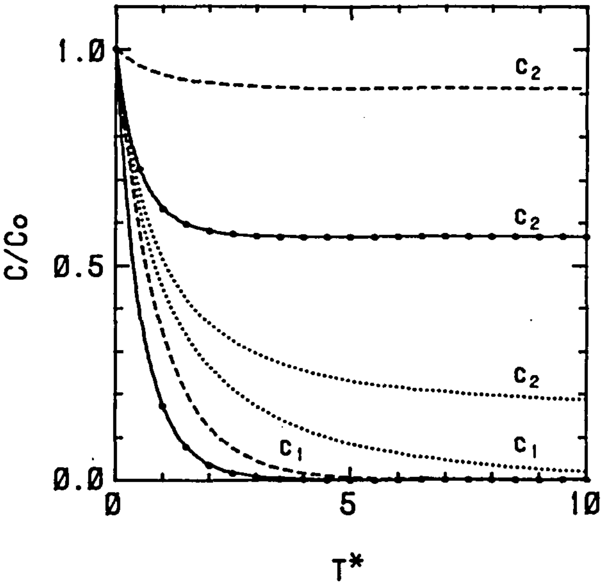

Fig. 3 Concentration profile with respect to normalized time, $T^* = k_{12}t$ for Case III. $R_1 = R_2 = 1$ and $k_1 = k_{12}$ for the solid line. $R_1 = R_2 = 1$ and $k_1 = 0.1k_{12}$ for the dotted line. $R_1 = 1$, $R_2 = 10$ and kl = 0.1k12 for the dashed line. The dots on the solid lines indicate the concentrations obtained by finite difference.

for the other is lower than the R_1=R_2 case because of the larger value of the right-most term of Eq. 21 (i.e. a larger sink).

CONCLUSIONS

The mass transport equations including the second-order coupled reaction mechanism have been derived producing coupled nonlinear partial differential equations. For batch-reactor systems with no concentration gradients several analytical solutions to the coupled ordinary differential equations have been found and illustrated by example. Several approachs to solving the coupled transport equations have been described and may give a direction for finding other analytical solutions to the transport equations which include second-order reaction.

If the second-order reaction mechanism is used as a soil-water reclamation method, and C_2 is considered the pollutant, the concentration profile, amount of C_1 required to adequately reduce the concentration of C_2 to below prescribed limits and the time necessary to do so can be obtained from the solution of Eq. 7. It is believed that using the second-order reaction mechanism can offer additional methods for analyzing reclamation alternatives of polluted soil-water systems.

To use Eq. 7 a value of k_{12} for the second-order reaction (see Eq. 1) must be obtained. The solutions provided herein may be used to evaluate batch reactor data to obtain a value for k_{12} whether neither, one or both species undergo first-order decay provided that the (first-order) decay constant and the retardation coefficients are known a priori.

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APPENDIX

LIST OF SYMBOLS

Symbol	Description	Units
C_{ia}, C_i	concentration in aqueous phase for specie i	$M\ M^{-1}$
C_{is}	concentration in solid phase for specie i	$M\ M^{-1}$
D_{ia}, D_i	diffusion-dispersion in aqueous phase for specie i	$L^2\ T^{-1}$
k_i	lumped transformation rate	T^{-1}
k_{ias}	first order transfer coefficient aqueous to solid phase for specie i	T^{-1}
k_{isa}	first order transfer coefficient solid to aqueous phase	T^{-1}
k_{id}, k'_{id}	unitless soil-water partition coefficient	
k_{ita}	first order transformation rate aqueous phase	T^{-1}
k_{its}	first order transformation rate solid phase	T^{-1}
$\bar{k}_{12}$	second-order reaction constant coefficient	$L^3\ TM^{-1}$
V_{ia}, V_i	interstitial velocity of aqueous phase	$L\ T^{-1}$
θ	volume fraction occupied by the aqueous phase	
ρ_a	density of aqueous phase	$M\ L^{-3}$
ρ_b	bulk density of the soil	$M\ L^{-3}$

DEFINITIONS

$\alpha_1 = k_1/R_1$ $\alpha_2 = k_2/R_2$ $\alpha = k_1/R_1 = k_2/R_2$

$\beta_1 = k_1/V_1$ $\beta_2 = k_2/V_2$ $\beta = k_1/V_1 = k_2/V_2$

$\gamma_1 = V_1/R_1$ $\gamma_2 = V_2/R_2$ $\gamma = V_1/R_1 = V_2/R_2$

$\varepsilon_1 = k_{12}/R_1$ $\varepsilon_2 = k_{12}/R_2$ ε = see Eq. 2

$\lambda_1 = k_1/R_1$ $\lambda_2 = k_2/R_2$ $\lambda = k_1/R_1 = k_2/R_2$

$\xi_1 = t - x/\lambda_1$ $\xi_2 = t - x/\lambda_2$ $\xi = t - x/\lambda$

$\varepsilon_3 = k_{12}/V_2$

a, b, d, f and g are locally defined (i.e. have different meanings for each case).

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