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### Authors

McNab, W.W.  
Narasimhan, T.N.

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## EARTH SCIENCES DIVISION

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December 1989

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**First-Order Kinetics-Controlled Multiple Species  
Reactive Transport of Dissolved Organic Compounds in  
Groundwater: A Numerical Model**

*W. W. McNab, Jr., and T. N. Narasimhan*

Earth Sciences Division  
Lawrence Berkeley Laboratory  
University of California  
Berkeley, California 94720

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# First-Order Kinetics-Controlled Multiple Species Reactive Transport of Dissolved Organic Compounds in Groundwater: A Numerical Model

*W. W. McNab, Jr. and T.N. Narasimhan*

Earth Sciences Division  
Lawrence Berkeley Laboratory  
University of California, Berkeley  
1 Cyclotron Road  
Berkeley, CA 94720

## ABSTRACT

*Reactive chemical transport models developed over the past decade have generally relied on the assumption that local thermodynamic equilibrium is achieved at all times between aqueous species in a given system. Consequently, systems characterized by kinetically slow reactions, particularly problems involving organic species, cannot be satisfactorily modeled. In this study, we present a prototype computer model, KINETRAN, which is designed to handle kinetically-controlled homogeneous reactions in the aqueous phase, along with the transport of the various species involved, through geologic media.*

*The kinetics algorithm allows a number of user-specified homogeneous reactions to simultaneously approach overall equilibrium under the control of first-order reaction kinetics. We achieve this by discretizing the first-order rate equations, using a time-averaging factor, for all of the aqueous-phase reactions, both forward and backward. The resulting set of implicit, linear equations is solved through the use of matrix algebra.*

*The kinetics algorithm is dynamically coupled with a transport model that explicitly solves the advection-diffusion-dispersion equation, with adsorption being handled through the use of retardation coefficients. The transport equations are solved according to the Integral Finite Difference Method (Narasimhan and Witherspoon, 1977). The coupling with the kinetics equations is accounted for through the use of source terms.*

*We apply this model to a hypothetical problem involving the simultaneous transport and chemical degradation of two halogenated hydrocarbons through a one-dimensional soil column. The results of the modeling study show that the transient species produced as*

*intermediate products of the degradation of the halogenated hydrocarbons occur in significant amounts before they too are degraded. This phenomena, which is known to occur in the field, has received little attention in previous modeling studies. More important, the simulation results show that the model is mathematically internally consistent and produces credible results given the input data.*

*The credibility of this modeling approach paves the way for handling realistic field problems involving kinetically-controlled reactive chemical transport of organic compounds. Additionally, the model might be useful under certain favorable circumstances to back-out, by the process of calibration, kinetics parameters that are difficult to determine in the laboratory or are otherwise unavailable.*

## 1. INTRODUCTION

### 1.1. Motivation.

Numerous reactive chemical transport models have appeared in the literature in recent years for simulating chemical transport in groundwater systems. Essentially, these solve the classical advection-diffusion-dispersion equation, coupled with appropriate equations for reactions involving thermodynamic equilibrium among the various species involved. Liu (1988) and Liu and Narasimhan (1989a) provide a summary of some of the more recent work in this field.

Many of the reactive transport models that are currently available are designed to solve problems of a geological interest, although some are geared to applied, engineering-oriented problems. Because the time scales involved in geological problems are generally very large compared to chemical reaction times, the assumption of local thermodynamic equilibrium, at least among the aqueous species, is often an acceptable approximation. This is the basis for the use of equilibrium geochemical models such as PHREEQE (Parkhurst et al., 1980) and EQ3/EQ6 (Wolery, 1979, 1983) to handle heterogeneous interactions in reactive transport models (Ague, 1987 and Liu and Narasimhan, 1989a). Problems that are highly dependent on mineral dissolution reactions cannot always be studied with pure equilibrium chemistry models, thus attempts at including mineral dissolution kinetics in reactive transport models have been made (Ague, 1987 and Liu, 1988). These attempts at incorporating non-equilibrium effects have focused on heterogeneous interactions. With rare exceptions, the kinetics of homogeneous reactions in the aqueous phase have so far received little attention in the literature in relation to transport modeling.

Aqueous systems in which the reaction times between the various reactive species present become significant compared to the overall simulation time require that non-equilibrium effects be duly considered. Systems with dissolved organic species frequently involve reactions with high activation energies which often have low reaction rates under normal environmental conditions. Of particular environmental concern are the degradation reactions that determine the eventual fate of organic industrial solvents and petroleum products that find their way into groundwater. Equilibrium-based reactive transport models are not capable of simulating these systems with adequate detail and accuracy to assist in designing efficient remedial strategies.

To illustrate this point, consider the following hypothetical problem. A small amount of dissolved methyl chloride and methyl bromide are added to a fully-saturated soil or rock mass with background concentrations of dissolved carbon dioxide, free chloride, and free bromide.

Both compounds are normally found as gases at standard temperature and pressure, but they are slightly soluble in water. These halogenated hydrocarbons were chosen for this illustration because of their relatively simple chemistry; only a small number of possible degradation reactions exist. Both compounds may undergo hydrolysis reactions that produce methyl alcohol and free halogen ions (Mabey and Mill, 1978). However, under very reducing conditions methane may be produced, while under more oxidizing conditions, microbes may assist in converting the materials into formaldehyde (Vogel et al., 1987). Alcohol and formaldehyde may in turn be oxidized into formic acid (Hart, 1987). In addition, all of these "daughter" hydrocarbons, methane, alcohol, formaldehyde, and formic acid, will themselves be eventually oxidized to carbon dioxide under oxidizing conditions.

Bearing these possibilities in mind, we define the following initial conditions in the groundwater. All concentrations † are given in moles per liter:

$$\begin{aligned}[\text{CH}_3\text{Cl}(\text{aq})] &= 10^{-4} \\[\text{CH}_3\text{Br}(\text{aq})] &= 10^{-4} \\ \text{total } [\text{CO}_2(\text{aq})] &= 10^{-3} \\ [\text{Cl}^-] &= 10^{-3} \\ [\text{Br}^-] &= 10^{-10}\end{aligned}$$

The initial concentrations of the other species (methane, methyl alcohol, formaldehyde, formic acid) are set equal to zero. The pH of the system is assumed to be buffered at 7.0 by the mineral species present in the soil matrix and by inorganic species in the aqueous phase. Aqueous complexing with inorganic species is not considered. All activity coefficients are assumed to be unity. A temperature of 25 ° C is assumed. Given these initial conditions, and the thermodynamic data describing this system (see Appendix A), the final equilibrium state of all of the species of interest can be calculated by a simple iterative technique, which will be described later.

Figures 1 and 2 show the equilibrium concentrations of the various hydrocarbon species as a function of Eh. Clearly, methane is the dominant species present under reducing conditions, whereas carbon dioxide is the significant species under oxidizing conditions. All of the

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† Throughout this paper, we use square brackets "[ ]" to denote concentrations as well as activities, since the two are approximately equal in dilute solutions because the activity coefficients will essentially be equal to unity.



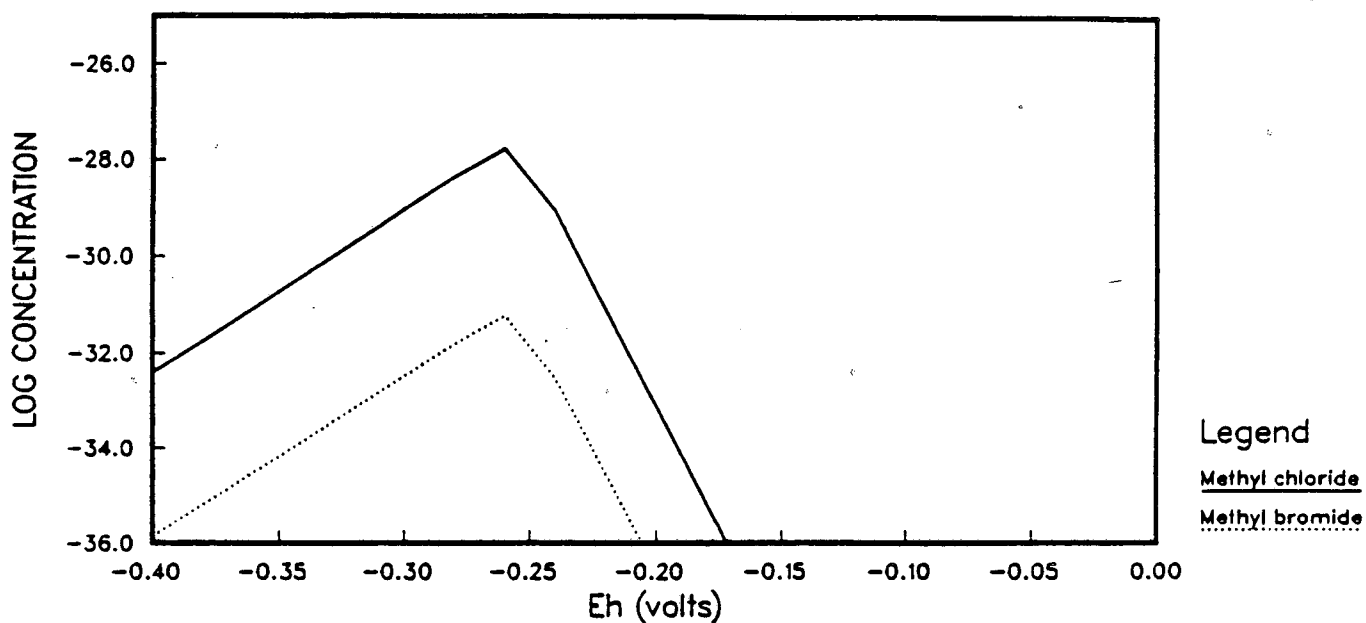


Figure 1. Hypothetical log concentrations (moles/liter) of methyl chloride and methyl bromide as a function of Eh at a pH of 7.0 and at 25 ° C.

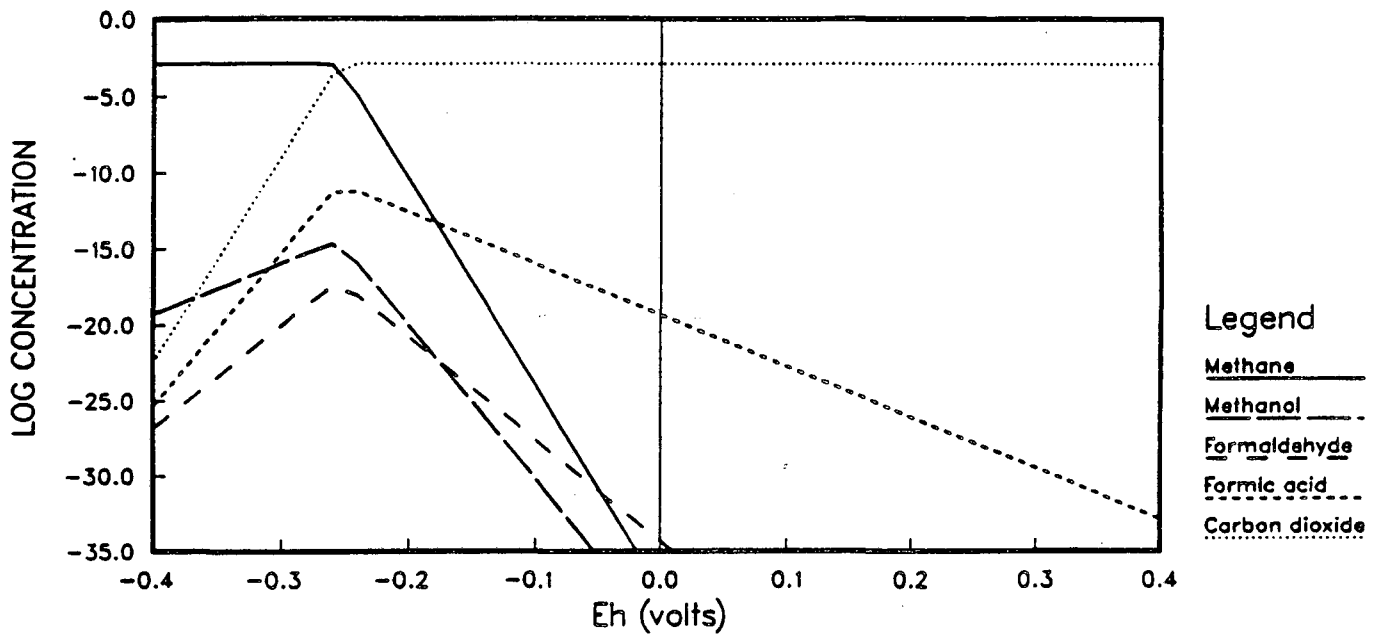


Figure 2. Hypothetical log concentrations of organic species involved in the degradation of methyl chloride and methyl bromide as a function of Eh.

other species occur in trivial (essentially zero) amounts. This is particularly true of the primary pollutants, methyl chloride and methyl bromide. These results are, of course, quite reasonable since carbon dioxide is ubiquitous in most groundwater environments, while methane is found in very reducing environments, isolated from atmospheric oxygen. Methyl alcohol, formaldehyde, and formic acid are not found in natural sediments.

The problem with the above instantaneous equilibrium approach is that it shows the state of the system that would exist only after a considerable amount of time has passed. For very slow reactions, this may mean hundreds or even thousands of years. If this model is used to solve reactive transport problems involving hydrocarbon pollutants, the pollutant concentrations would fall to essentially zero instantaneously after the transport process begins and only CO<sub>2</sub> or CH<sub>4</sub> will remain and be transported through the system. However, the persistence of halogenated hydrocarbons in carefully monitored polluted groundwater systems indicates that the establishment of equilibrium between the introduced constituents involves time. Therefore, the equilibrium approach must be abandoned in favor of a technique that treats the final equilibrium state of the system only as a "goal" for the various species involved to tend towards over a finite time period, a process governed by reaction kinetics.

## 1.2. Purpose and Scope.

The purpose of this study is to develop a numerical model for the transformation and transport of aqueous species that dispenses with the assumption of instantaneous equilibrium. Such a model would solve for the spatial and temporal changes in concentration of a number of interacting species due to the effects of transport and kinetically-controlled chemical transformations within a given groundwater environment. If successful, such a model would be of value not only to contaminant transport hydrology but also to other branches of earth science as well, such as in the study of the evolution of petroleum reservoirs.

We introduce a model, KINETRAN (KINETically-controlled reactive chemical TRANsport), in an attempt to meet this goal. In this paper, the development of this model is discussed, with special emphasis on the theoretical basis of the kinetics algorithm. (We must emphasize that the model treats all kinetically-controlled transformation processes as *black-box* processes. No attempt is made to distinguish between abiotic degradation, such as hydrolysis reactions, and biodegradation.) The model is applied to a hypothetical one-dimensional problem in order to verify its mathematical consistency and to illustrate its applicability.

It is important to recognize that numerical models of chemical transport are not absolute predictive tools. Rather, they are devices that enhance our understanding of how complex natural systems may behave in response to different contamination scenarios. This is

especially true of the type of problems of interest here because some of the parameters needed for the simulation, particularly the first-order kinetic rate constants, may not be known *a priori*. Indeed, these quantities are known to be dependent on such factors as the presence of catalysts and the type and amount of microbes present in the system. The parameters are thus system-dependent. The fact that the relevant kinetic parameters are not known *a priori* may be viewed by some as a very significant impediment to the applicability of the algorithm to realistic field problems of interest. We, however, feel that this lack of data on parameters may in fact enhance the utility of such an algorithm as KINETRAN in that, given carefully collected field data, the model can be used as part of a history-matching scheme to "back-out" acceptable kinetic coefficients for certain systems. The parameters obtained by this calibration technique may indeed prove to be of greater practical value than those estimated from laboratory experiments carried out under highly idealized conditions. Such data may prove to be of use at other sites where field conditions are of a similar nature.

The present version of KINETRAN is strictly a prototype intended to test the feasibility of a concept. As of now, it is restricted to dilute solutions. Immiscible flow phenomena and volatilization are ignored. The concentrations of all species present are assumed to be low enough so as not to affect the physical properties of the solvent, namely water. No attempt is made to calculate activity coefficients; all are assumed to be unity. The activity of water is also taken to be unity.

The pH and Eh of the system are allowed to vary spatially, but are treated as constant in time. In other words, the pH and Eh at any given location in the system are assumed to be buffered by the existing mineral assemblage in the soil and by inorganic aqueous species, such as, for example, the  $\text{Fe}^{2+} - \text{Fe}^{3+}$  redox couple. The relative slowness of many hydrocarbon reactions, and the dilute solution assumption, suggest that this is probably a reasonable assumption.

Additionally, other than adsorption, no heterogeneous reactions are considered. That is, any mineral phases present affect the aqueous phase *only* by buffering the pH and Eh at constant values.

The program is capable of handling adsorption through the use of distribution coefficients. Adsorption is assumed to affect the system only by retarding the flux of the various species involved. Thus, the chemical kinetics algorithm treats sorbed species in exactly the same manner as their aqueous counterparts with regard to the rate and extent of any chemical reactions that occur. The alternative approach would be to model the adsorption process with the use of a sink term in the transport equation. In this case, sorbed species would simply remain part of the solid phase, removed from the aqueous phase and unable to undergo any aqueous chemical transformations. Presently, enough experimental data are not available to

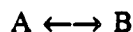
suggest precisely how sorbed organic species might behave chemically under realistic environmental conditions. It could well be that the process of adsorption itself may catalyze some of the degradation reactions with which we are concerned. For example, the interstices of some clay minerals may serve as sites which promote hydrolysis reactions of some organic species (Apps, 1989). This is clearly an area where further research is warranted.

Finally, the present model simulates only completely isothermal systems. For advective transport, the model is restricted to a steady fluid flow field.

## 2. THEORETICAL BASIS

### 2.1. First-Order Kinetic Processes.

Consider a system which contains only two hypothetical species, A and B, and a solvent in which they are dissolved, water. The only possible reaction that can take place in this system is the reversible reaction



Neglecting activity coefficients, at equilibrium, the concentrations of the species will satisfy the relation,

$$\frac{[B]}{[A]} = K_{eq} \quad (1)$$

where  $K_{eq}$  is the equilibrium constant. Obviously, if any given initial concentrations for A and B do not satisfy (1), this reaction will be driven in the direction that favors equilibrium. The net rate at which such a reaction will proceed is equal to the forward rate minus the reverse rate. These reaction rates, considered separately, often approximately follow first-order kinetics. Thus,

$$\frac{d[A]}{dt} = -k_1[A] \quad (2)$$

$$\frac{d[B]}{dt} = -k_2[B] \quad (3)$$

Chemical equilibrium is, of course, not a static equilibrium but a dynamic one. When the system is far from equilibrium, reaction in one direction will dominate, but as equilibrium is approached the opposite reaction becomes significant. Finally, once equilibrium is established, the forward and reverse reaction rates must be equal. Hence,

$$\frac{d[A]}{dt} = \frac{d[B]}{dt}$$

Therefore, from (2) and (3),

$$k_1[A] = k_2[B]$$

So, at equilibrium,

$$k_2 = k_1 \frac{[A]}{[B]} \quad (4)$$

However,  $[A]/[B]$  is already shown by (1) to be the reciprocal of the equilibrium constant, thus we find that the rate constant for the reverse reaction is related to that for the forward reaction by,

$$k_2 = \frac{k_1}{K_{eq}} \quad (5)$$

Therefore,  $k_1$ ,  $k_2$ , and  $K_{eq}$  are mutually related. This very simple exercise, in fact, forms an important element in the logic of the kinetics-solving algorithm in KINETRAN. If one has an estimate for the value of  $K_{eq}$ , and an estimate for  $k_1$ , the kinetic coefficient for the dominant initial reaction direction, then  $k_2$  can be calculated from an expression such as (5).

As long as first-order kinetics are assumed, the above technique can be used for determining  $k_2$  for more complicated reactions. For example, suppose that the reaction between A and B is actually an oxidation reaction such that



where  $H^+$  denotes a free hydrogen ion,  $e^-$  denotes a hypothetical † free aqueous electron, and C refers to some other species. Now,

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† The quantity  $[e^-]$ , which we refer to throughout this paper, does not refer to the actual concentration of free aqueous electrons, which is essentially zero. Rather, it is a purely hypothetical concentration which is a reflection of the redox state of the system. Without going through the derivation (Thorntson, 1984), we state here that  $[e^-] = 10^{-(pE)}$ , where  $pE = Eh(F/2.303RT)$ ,  $Eh$  = electrical potential with reference to the standard hydrogen electrode,  $F$  = Faraday constant,  $R$  = Universal Gas Constant, and  $T$  = temperature in Kelvin.

$$\frac{[B]^3[H^+][e^-][C]}{[A]} = K_{eq}$$

Also, we assume a rate dependence on [B] only,

$$\frac{d[B]}{dt} = -k_2[B]^3$$

As we will show later, rate law expressions other than first-order will lead to a system of non-linear equations. In order to avoid this difficulty and maintain a system of linear equations, we linearize this equation by using the approximation,

$$k'_2 \approx k_2[B]^2$$

Thus,

$$\frac{d[B]}{dt} \approx -k'_2[B]$$

We see that by analogy to (4)

$$k'_2 = k_1 \frac{[A]}{[B]}$$

From the equilibrium condition,

$$\frac{[A]}{[B]^3} = \frac{[H^+][e^-][C]}{K_{eq}}$$

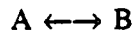
Substituting this expression into (4), which relates the forward and reverse rate constants to each other, we find

$$k'_2 = k_1 \frac{[H^+][e^-][C][B]^2}{K_{eq}}$$

Even in this case,  $k'_2$  may still be determined if we assume that the pH and Eh are held constant and that we can calculate [B] and [C] at equilibrium from thermodynamic considerations.

## 2.2. Solution Techniques.

Consider again the reaction



If we look at only the forward reaction, we note that

$$\frac{d[A]}{dt} = k_1[A]$$

may be integrated in order to solve for the concentration of A after an interval of time  $\Delta t$  has elapsed:

$$[A] = [A_0]e^{-k_1\Delta t} \quad (6)$$

where  $[A_0]$  is the concentration of A at the beginning of  $\Delta t$ . Equation (6) will accurately represent the temporal evolution of  $[A]$  if the reaction is far from equilibrium. However, as the reaction approaches equilibrium, species A will begin to be produced in significant amounts by the reverse reaction  $B \rightarrow A$ . This newly produced A will itself begin to react to form B again, and so on. Thus, the quantity  $[A_0]$  in (6) becomes ambiguous as equilibrium is approached. If the system is more complex, with additional species present and many reactions occurring, with each species being involved in a number of possible reactions, the problem is greatly compounded. If one chooses to model this system by sequentially solving a number of explicit equations such as (6) for all of the possible forward and reverse reactions, very small time steps must be taken in order to achieve accuracy as the reactions approach equilibrium. If the simulation time is large, this could prove to be computationally inefficient.

Clearly, if  $i$  species are present in a system, there exists a strong motivation to find a method for simultaneously solving for all  $\Delta c_i$  over a given  $\Delta t$ , where  $c_i$  is the aqueous concentration of species  $i$ . This can be achieved by using a time-averaging discretization scheme analogous to those used in the time-integration of transient diffusion processes such as heat conduction or groundwater flow using numerical methods. Such a solution technique is as follows. First, instead of directly integrating the rate equation, discretize it. Thus,

$$\frac{\Delta[A]}{\Delta t} = -k_1[\bar{A}] \quad (7)$$



where  $[\bar{A}] = [A_0] + \lambda\Delta[A]$ , an effective average value for  $[A]$  over the given time interval  $\Delta t$ . The task here is to choose a value for  $\lambda$  that will allow the discretized equation to very closely approximate the differential rate equation. Note that in the modeling of transient diffusion processes,  $\lambda = 0.0, 0.5,$  and  $1.0$  are respectively known as Forward-Differencing, Central-Differencing, and Backward-Differencing schemes.

By definition, the change in concentration  $\Delta[A]$  over a time interval  $\Delta t$  is,

$$\Delta[A] = [A] - [A_0] = [A_0]e^{-k_1\Delta t} - [A_0] \quad (8)$$

According to (7), the discretized rate equation, we wish to approximate this relation,

$$\Delta[A] = -k_1 \left[ [A_0] + \lambda\Delta[A] \right] \Delta t \quad (9a)$$

Rearranging this equation in terms of  $\Delta[A]$ , we find,

$$\Delta[A] = \frac{-k_1 A_0 \Delta t}{k_1 \lambda \Delta t + 1} \quad (9b)$$

Equating (8) and (9b), we obtain

$$\lambda = \frac{1}{1 - e^{-k_1\Delta t}} - \frac{1}{k_1\Delta t} \quad (10)$$

Thus, the approximation for  $\lambda$  depends only on the value of  $k$  (forward or reverse reaction), and the time step. Therefore, a precise value for  $\lambda$  can be calculated for every reaction in the system (forward or backward) in order to achieve maximum overall accuracy.

Using this method, one can write an expression  $\Delta c_i$  for every reaction for every species  $i$  in the system. Collecting the terms eventually yields a linear system of  $i$  unknowns and  $i$  equations, which can be solved for  $\Delta c_i$  for all species in the system over  $\Delta t$ . We discuss the process of setting up these equations in the following sections.

## 2.3. The Kinetics Equations.

### 2.3.1. Equilibrium Calculations.

Earlier, we showed that for general first-order kinetic reactions, we need to know the final equilibrium state of the system in order to calculate the kinetic coefficients in the reverse, or initially non-dominant directions. For relatively simple systems, this step in the model may seem trivial. For example, for a system containing chlorinated hydrocarbons, only concentrations such as  $[Cl^-]$  at equilibrium would need to be predicted, which would essentially be equal to the total chlorine concentration.  $[H^+]$  and  $[e^-]$  would already be externally fixed, and thus these need not be determined either. However, for more complicated systems involving complex interactions among organic species, an equilibration routine is essential. This is true of inorganic species as well. If sulfur is present as a component, for example, the equilibration routine would be needed to determine the relative concentrations of  $SO_4^{2-}$ ,  $S^{2-}$ , or  $HS^-$  as a function of pH and Eh. Therefore, before we proceed with assembling the equations which describe the kinetically-controlled reactions, we present a method for determining the final equilibrium concentrations of the equilibrating species. Given the necessary equilibrium constants (see Appendix A), it is relatively simple to calculate this if the pH and Eh of the system are held constant, which we assume.

Many well-known geochemical simulators, PHREEQE (Parkhurst et al., 1980) and EQ3NR (Wolery, 1983), determine aqueous speciation through the use of mass action and mass balance equations which constrain the possible final equilibrium state of a given system of aqueous species. Because of the extremely high concentration of water relative to any other species present in most problems, implementation of the mass balance constraint for the elements H and O is generally not feasible. Because of this, the mass balance equations for these two elements are replaced by charge balance and electron balance equations, respectively. Eventually, a set of highly non-linear equations is developed which may contain terms that differ from one another by many orders of magnitude, requiring fairly sophisticated mathematical techniques for solution. For this purpose, Newton-Raphson iteration is a preferred method, with the starting estimates obtained by various optimization schemes (Parkhurst et al., 1980). However, because we choose to hold the pH and Eh constant, thus holding  $[H^+]$  and  $[e^-]$  constant, in the present work we eliminate the need to solve a charge balance and an electron balance equation. This permits us to use a far simpler iteration scheme that is quite fast and is generally very reliable.

To illustrate this technique, consider again the hypothetical equilibration problem described section 1.1. There are three components present (aside from hydrogen and oxygen) that make up the system: carbon, chlorine, and bromine. These three give rise to the nine

species that participate † in the degradation reactions:

methyl chloride, CH<sub>3</sub>Cl(aq)  
methyl bromide, CH<sub>3</sub>Br(aq)  
methane, CH<sub>4</sub>(aq)  
methyl alcohol, CH<sub>3</sub>OH  
formaldehyde, HCHO  
formic acid, HCOOH  
total carbon dioxide, CO<sub>2</sub>(aq)  
free chloride, Cl<sup>-</sup>  
free bromide, Br<sup>-</sup>

Under externally fixed pH and Eh values, the final equilibrium state of the system is entirely defined by mass action equations between the various species and by mass balance constraints on the total amount of each element present. As a first step, we define a set of *master species* such that each element is represented by an appropriate species which is used in the mass action equations. The master species chosen for each element should be species whose equilibrium concentration is relatively large over a wide range of pH and Eh values and which never falls below the underflow tolerance of the computer system being used. Referring again to Figures 1 and 2 and using these criteria, we chose CO<sub>2</sub> as our master species for carbon, Cl<sup>-</sup> for chlorine, and Br<sup>-</sup> for bromine. Of course, H<sup>+</sup> and e<sup>-</sup> are actually master species, representing H and O, respectively.

Next, we assign each of the master species a concentration value corresponding to the total amount of that element present. Thus, we define the *virtual* concentration of a master species to be equal to the sum of the concentrations of each compound in which the given element occurs times its stoichiometric coefficient. For our example,

$$[\text{CO}_2]^* = [\text{CH}_3\text{Cl}] + [\text{CH}_3\text{Br}] + [\text{CH}_4] + [\text{CH}_3\text{OH}] + [\text{HCHO}] + [\text{HCOOH}] + [\text{CO}_2]$$

$$[\text{Cl}^-]^* = [\text{CH}_3\text{Cl}] + [\text{Cl}^-]$$

$$[\text{Br}^-]^* = [\text{CH}_3\text{Br}] + [\text{Br}^-]$$

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† Other species are present in the simulation but are not included in this list. H<sup>+</sup> and e<sup>-</sup> are involved in many of the reactions but are externally fixed at constant values. H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub><sup>-</sup>, and CO<sub>3</sub><sup>2-</sup> are also present but are considered separately since the degradation reactions are written in terms of CO<sub>2</sub>(aq).

Also,

$$[H^+] = 10^{-pH}$$

$$[e^-] = 10^{-pE}$$

The ratio of the equilibrium concentrations of the non-master species to the master species are then determined through mass action equations. For example, consider the reaction,



Because the activity of water is taken to be unity, we may write the mass action equation as,

$$\frac{[CO_2(aq)][H^+]^6[e^-]^6}{[CH_3OH]} = K_{eq} = 10^{-4.619}$$

Therefore, we can express the virtual  $[CH_3OH]$  as a function of the master species concentrations by,

$$[CH_3OH]^* = \frac{[CO_2(aq)]^*[H^+]^6[e^-]^6}{K_{eq}}$$

We proceed to solve mass action equations such as this for all of the non-master species present. This yields the relative, or virtual, concentrations of all of the species, but not the absolute concentrations, as mass must be conserved. To correct for this, we convert the virtual concentrations into absolute concentrations by using a normalization factor  $v$ . To calculate  $v$  for a given component, we first take the sum of the total virtual concentration of the component. Thus,

$$x = \sum_{s=1}^S \mu_{i,s} [s_i]$$

where  $[s_i]$  is the virtual concentration of species  $s$  which contains component  $i$ , and  $\mu_{i,s}$  is the stoichiometry of component  $i$  in species  $s$ . For example, for carbon in this study,

$$x = [CH_3Cl]^* + [CH_3Br]^* + [CH_4]^* + [CH_3OH]^* + [HCHO]^* + [HCOOH]^* + [CO_2]^*$$

But we know the initial amount of total carbon, or any other component, that is present, thus we can define the normalization factor  $v$  such that

$$v = \frac{\text{total initial carbon}}{x}$$

We then multiply all of the species containing carbon by  $v$  to obtain an estimate of their absolute concentrations. The same process is followed for chlorine and bromine.

If only one element is present (other than H and O), this scheme will yield the correct solution directly, without iteration. If other elements are present, however, the above procedure (following the definition of the master species) must be performed several times until all of the species concentrations are satisfied to within a specified convergence tolerance.

Additionally, once the kinetics equations are solved, reactions that are assumed to take place instantaneously, such as the speciation of  $\text{CO}_2$  into  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ , as well as  $\text{HCOOH}$  into  $\text{HCOO}^-$ , can be calculated after the kinetics equations are solved, using this scheme.

We have already emphasized that KINETRAN assumes constant pH and Eh values at a given location throughout the simulation. It is possible to circumvent this restriction by simply inserting a charge balance and an electron balance equation into the above iteration scheme and treating  $[\text{H}^+]$  and  $[\text{e}^-]$  as dependent variables. This is actually quite easy to do but is not appropriate to implement for two reasons. The first is strictly chemical: introducing this feature will cause the pH and Eh of the system to depend *entirely* on the degradation of the organic species present, and not at all on the mineral assemblage and the inorganic species present. In almost every conceivable scenario, this is probably a very poor assumption. Secondly, additional computational features such as Newton-Raphson iteration schemes would need to be incorporated in order to assure convergence of the solution, unnecessarily increasing the complexity and workload of the computer program.

### 2.3.2. Calculation of Parameters.

Once the final equilibrium concentrations for all species of interest in the system have been calculated on the basis of the equilibrium constants and the initial concentrations, the kinetic coefficients of the reverse reactions can be determined using the scheme outlined in section 2.1.

Because all the reactions that are allowed to take place under the control of first-order kinetics are completely user-defined, it is somewhat arbitrary as to the direction in which a

reaction is written. Using the equilibrium constraint, the model determines the correct rate constant for the reverse reaction. In general, however, most reactions will have a dominant direction initially if they are far from equilibrium, and the kinetic rate constant for this forward reaction is usually the most well-known, so it is convenient to use this as the preferred direction.

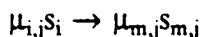
Recall that in order to implicitly solve the simultaneous reaction problem, we defined a time-averaging parameter,  $\lambda$ . A separate value for  $\lambda$  must be determined for every reaction, forward and backward. This is easily accomplished by setting up an indexing system for  $\lambda$  and using (10) to directly estimate it from the rate constant for the reaction and the time step  $\Delta t$ .

It is possible that in many situations, the kinetic coefficients for various reactions will not be constant but may depend, for example, on the number of microbes present. The present version of the KINETRAN model does not directly consider this possibility. However, these phenomena could be handled by inserting conditional statements into the program that allow the kinetics parameters to vary with time or with other controlling factors such as microbe populations.

### 2.3.3. Assembling the Matrix of Equations.

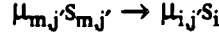
Once the reverse-direction reaction rates and  $\lambda$ -parameters have been calculated, it is relatively straightforward to set up a set of linear equations that can be solved for all  $\Delta c_i$ .

We know that among all of the aqueous species present in the simulation, a certain number of reactions will take place. For any given species over a given time step, there will be sink terms, where the species is destroyed in some reactions, and source terms, where it is created in others. If we look back at our example from section 2, we note that the reaction  $A \rightarrow B$  destroys A and creates B, while the reverse reaction  $B \rightarrow A$  likewise destroys B and creates A. A separate equation analogous to (9a) can be written for  $\Delta c_{ij}$  for every reaction  $j$  that involves species  $i$ . We define  $\Delta c_i$  to be a positive quantity when it is produced in a reaction, and negative when consumed. Thus, if we write all the reactions of interest proceeding in the initially dominant direction, then for a given species  $i$ , there will be  $J_r$  reactions in which it is a reactant that is destroyed, and  $J_p$  reactions in which it is a generated as a product. If we define  $s_i$  as species  $i$  and  $s_{m_j}$  as the complementary species that is produced or destroyed, depending on reaction direction, with species  $i$  in reaction  $j$ , then we have, when  $i$  is a reactant,



for  $j = 1, 2, 3, \dots, J_r$ , where  $\mu_{ij}$  and  $\mu_{mj}$  refer to the respective stoichiometric coefficients.

When  $i$  is written as the product of a reaction, then



where  $j' = 1, 2, 3, \dots, J_p$ . Taking all possible reactions into account, we find,

$$\Delta c_i = \Delta t \sum_{j=1}^{J_r} \frac{\mu_{i,j}}{\mu_{m,j}} k_{j,r} [c_{m,j}^0 + \lambda_{j,r} \Delta c_{m,j}] - k_{j,f} [c_i^0 + \lambda_{j,f} \Delta c_i] +$$

$$\Delta t \sum_{j'=1}^{J_p} \frac{\mu_{i,j'}}{\mu_{m,j'}} k_{j',f} [c_{m,j'}^0 + \lambda_{j',f} \Delta c_{m,j'}] - k_{j',r} [c_i^0 + \lambda_{j',r} \Delta c_i]$$

Here,  $c_i$  and  $c_{m,j}$  refer to the concentrations of  $s_i$  and  $s_m$ , respectively. The subscripts  $f$  and  $r$  refer to the forward and reverse reactions, respectively.

The equation presented above is written for each species  $i$  present in the system. It summarizes the changes in concentration of species  $i$  due to production in reverse reactions, destruction in forward reactions, production in forward reactions, and destruction in reverse reactions, respectively. Because of the unknown terms present in each of these equations, the  $\Delta c_m$  values, the system of equations is implicit and must be solved through the use of matrix algebra. In order to accomplish this, the set of equations in the form given above are written in matrix form so that

$$[A_{i,m}][\Delta c_i] = [B_i] \quad (11)$$

We define the terms of this matrix in the following manner. Let the total number of reactions that occur in the system, between all of the species present, be  $N$ , so that  $n = 1, 2, 3, \dots, N$ . Also, when referring to any of these reactions, we introduce a variable  $d$  such that  $d = 1$  for the forward reaction and  $d = 2$  for the reverse reaction. It can be shown, through algebraic manipulation for our expression for  $\Delta c_i$ , that, for  $i = m$ ,

$$A_{i,m} = \Delta t \left[ - \sum_{n=1}^N k_{n(i,m),d} \lambda_{n(i,m),d} \right] - 1$$

where  $k_{n(i,m),d} = k_{n,1}$ , if  $i$  is written as a reactant in reaction  $n$

=  $k_{n,2}$ , if  $i$  is written as a product in reaction  $n$

= 0, if  $i$  is not involved in reaction  $n$ .

$\lambda_{n(i,m),d}$  is subscripted in a manner analogous to  $k$ .

For  $i \neq m$ ,

$$A_{i,m} = \frac{\mu_{i,n(i,m)}}{\mu_{m,n(i,m)}} \Delta t k_{n(i,m),2} \lambda_{n(i,m),2}, \text{ if } i \text{ is a reactant in reaction } n \text{ with } m$$

$$= \frac{\mu_{i,n(i,m)}}{\mu_{m,n(i,m)}} \Delta t k_{n(i,m),1} \lambda_{n(i,m),1}, \text{ if } i \text{ is a product in reaction } n \text{ with } m$$

= 0, if  $i$  does not react with  $m$ .

$\mu_{i,n(i,m)}$  and  $\mu_{m,n(i,m)}$  refer to the respective stoichiometric coefficients of species  $i$  and  $m$  in reaction  $n$ .

The "known" vector  $B_i$  is a function of the initial conditions. Here, we define  $B_i$  as,

$$B_i = \Delta t \left[ \sum_{n=1}^N k_{n(i,m),d} \right] c_i^0 - \sum_{n=1}^N B'_{n(i,m)} c_m^0$$

where  $k_{n(i,m),d} = k_{n,1}$  if  $i$  is a reactant in reaction  $n$

=  $k_{n,2}$ , if  $i$  is a product in reaction  $n$

= 0, if  $i$  is not involved in reaction  $n$ .

$$B'_{n(i,m)} = \frac{\mu_{i,n(i,m)}}{\mu_{m,n(i,m)}} \Delta t k_{n(i,m),2}, \text{ if } i \text{ is a reactant in reaction } n \text{ with } m$$

$$= \frac{\mu_{i,n(i,m)}}{\mu_{m,n(i,m)}} \Delta t k_{n(i,m),1}, \text{ if } i \text{ is a product in reaction } n \text{ with } m$$

= 0, if  $i$  does not react with  $m$ .



$c_i^0$  and  $c_m^0$  refer to the concentrations of species  $i$  and  $m$  at the beginning of time step  $\Delta t$ .

Eventually, after determining all of the terms according to the above procedure, we develop an  $i \times i$  matrix of linear equations, the unknowns being  $\Delta c_i$  and all of the other quantities, such as the kinetic coefficients,  $\lambda$ -parameters, and the initial values of  $c_i^0$  and  $c_m^0$  having been already calculated. The system of linear equations can then be conveniently solved by using an appropriate matrix solver.

Other species that take part in the given set of chemical reactions, but which are not included in the above formulation, are accounted for by using mass balance constraints after the matrix is solved. For example, for chloride,

$$\Delta c_{(\text{Cl}^-)} = \sum_{m'=1}^{M'} \mu_{m',\text{Cl}} \Delta c_{m'}$$

where  $M'$  represents the number of species containing chlorine atoms, and  $\mu_{m',\text{Cl}}$  is the stoichiometric coefficient for the number the chlorine atoms that are freed or taken up by species  $m'$  during reaction. The same approach is used for other species present, such as  $\text{Br}^-$ . Since the pH and Eh are fixed at constant values, changes in  $[\text{H}^+]$  and  $[\text{e}^-]$  as a result of the kinetically-controlled reactions need not be considered.

#### 2.4. The Transport Equation.

The kinetic rate equations described above have to be incorporated in the chemical transport equations. We now present these equations for a multiple species aqueous system. For convenience, we write these equations for a discrete elemental volume  $l$  communicating with its neighbors  $m$ , where  $m = 1, 2, 3, \dots, M$ . The complete equation describing chemical transport includes expressions for advection, molecular diffusion, hydrodynamic dispersion, adsorption, and source terms. Therefore, for species  $i$ ,

$$\sum_{m=1}^M q_{l,m} A_{l,m} \bar{c}_{l,m}^i + \sum_{m=1}^M n D_d^i \frac{\Delta c_{l,m}^i}{x_{l,m}} A_{l,m} + \sum_{m=1}^M n D_H^i \frac{\Delta c_{l,m}^i}{x_{l,m}} A_{l,m} + G_l^i = n V_{B,l} R^i \frac{\Delta c^i}{\Delta t} \quad (12)$$

Here, the first term on the left describes solute transport due to advection, where  $q_{l,m}$  is the volumetric fluid flux per unit area (darcy velocity) between  $l$  and  $m$  normal to the interface between them,  $A_{l,m}$  is the interface area, and  $\bar{c}_{l,m}^i$  is the average concentration of species  $i$  at the interface of the two volume elements.

The second and third terms on the left respectively describe molecular diffusion and hydrodynamic dispersion. Here,  $D_d$  and  $D_H$  are the diffusion and dispersion coefficients and  $n$  is the porosity of the material. The expression  $\Delta c_{l,m}^i/x_{l,m}$  is simply the concentration gradient of species  $i$  between  $l$  and  $m$  approximated according to the finite difference philosophy. When material heterogeneities are involved, the harmonic mean is used to obtain the spatially-averaged value for the one parameter. For example, for the diffusion coefficient,

$$D_d = \frac{x_l + x_m}{\frac{x_l}{D_{d,l}} + \frac{x_m}{D_{d,m}}}$$

where  $x_l$  and  $x_m$  refer to the respective distances from the nodal points to the interface and  $D_{d,l}$  and  $D_{d,m}$  refer to the respective diffusion coefficients for the two elements.

The final term on the left side of (12),  $G_l^i$ , is the source/sink term, which is an expression for net generation or destruction of species  $i$  in volume element  $l$ . This quantity is generally determined directly from evaluation of (11). However, if external sources or sinks for species  $i$  exist, they must also be included in this term. This includes mass-balance corrections to account for the creation of new cell mass material for microbe populations that may participate in biodegradation processes. The source/sink term is a crucial part of the KINETRAN algorithm, as this is the variable that provides the coupling between the transport and transformation equations.

Focusing on the right-hand-side of (12), the quantity  $V_{B,l}$  is the bulk volume of element  $l$ . The total change in concentration of species  $i$  during  $\Delta t$  is given by  $\Delta c^i$ . This is the *temporal* variation of concentration of the species in volume element  $l$  and should not be confused with  $\Delta c_{l,m}^i$  on the left-hand-side, which represents the *spatial* variation.

The variable  $R$  refers to the retardation coefficient, which is defined as

$$R^i = 1 + \frac{\rho_b K_d^i}{n}$$

Here,  $\rho_b$  is the dry bulk density of the matrix material and  $K_d^i$  is the distribution coefficient for species  $i$ . This expression describes the effect of adsorption on species  $i$ . Thus, adsorption influences the behavior of species  $i$  only by restricting its movement; no change in its chemical behavior is inferred. The alternative to this approach would be to include adsorption as part of the source/sink term. This would have implications for the chemistry of species  $i$ , as it would no longer be allowed to react in the aqueous phase. It is probable that a technique for

handling adsorption that is a hybrid of these two approaches would be the most realistic, but until more data are available on precisely how sorbed species behave chemically, implementing such an approach in the model would be premature.

Despite the fact that a relatively simple technique is utilized in the algorithm to handle adsorption, its influence on reactive chemical transport must not be viewed as a trivial matter, particularly with regard to organic species. Johnson et al. (1989) found, for example, that organic pollutants diffusing from a hazardous waste site into a surrounding clay liner were strongly sorbed, while inorganic species, such as  $\text{Cl}^-$ , were not sorbed at all. Thus, when using a model such as KINETRAN, one must be very careful in distinguishing adsorptive effects from purely homogeneous reactive effects.

The numerical modeling of the chemical transport portion of the KINETRAN algorithm reduces to solving (12) separately for every species in the system, for each volume element, over every time step. The equation is solved explicitly; that is, the advective, diffusive and dispersive fluxes are calculated using the initial values of concentrations for each time step in place of the time-averaged values. At the end of the time step,  $c_i$  is updated with  $\Delta c_i$ . In order to avoid unphysical oscillations, the explicit method must use time steps that are smaller than a critical time step. We state here, omitting the proof (Edwards, 1972 and Rasmuson et al., 1982) that

$$\Delta t_{\text{critical}} = \frac{\sum \text{Capacitance}}{\sum \text{Conductance} + \sum_{\text{upstream}} \text{Advectance}} = \frac{nV_{B,l}R}{\sum U_{l,m} + \sum_{\text{upstream}} F_{l,m}}$$

where  $U_{l,m} = n[D_d + D_H]A_{l,m} / D_{l,m}$  and  $F_{l,m}$  is the flux into  $l$  from  $m$ , where  $m$  is upstream from  $l$ . Advectance and conductance refer to the ability of the bounding surface of a volume element to advect and conduct solute into the element, respectively. The capacitance is simply the volume of fluid within the element times the retardation factor  $R$ . It is also of passing interest to mention here that the ratio of advectance to conductance,

$$\frac{\sum_{\text{upstream}} F_{l,m}}{\sum U_{l,m}}$$

is the generalized Peclet number for the volume element (Rasmuson et al., 1982).

Note that in the present work we first solve the transport equation and then the source/sink terms according to (11), volume element by volume element. This procedure is

analogous to the two-step procedure employed by Narasimhan et al. (1986) and Liu and Narasimhan (1989b) in solving redox-driven transport problems. In principle, we have a choice of solving the transport equation either by small time steps or without any restrictions on the time step if we use implicit methods. However, in order to minimize potential errors in temporal integration, we decided to use conservatively small time steps in accordance with the use of the explicit (forward-differencing) method. It is likely that we may be able to use larger values for  $\Delta t$  in conjunction with an implicit solution of the transport problem without much loss of accuracy. To what extent we can relax the size of the time step is as yet to be clearly understood.

### 3. APPLICATION

#### 3.1. Batch Simulation.

We first apply only the chemical transformation module of KINETRAN to the hypothetical problem presented in section 1.1. Transport of the various species involved is not considered. Using the same initial species concentrations, we fix the Eh at +0.1 Volts, the pH at 7.0, and the temperature at 25 ° C. The purpose of this exercise is to show how the concentrations of the various species involved evolve through time as compared to the instantaneous equilibrium case.

Possible pathways for the transformation of the methyl halide pollutants, as well as those of the secondary transient species, are shown in Figure 3. The set of reactions representing these transformations are shown in Table 1, along with the kinetic coefficients for the forward reactions. Almost all of these rate constants are, of course, estimated; but we believe that they will be more or less reasonable under some field conditions. For example, the rate constants for the two hydrolysis reactions are actual experimental values which seem to be constant over the neutral pH range at constant temperature (Mabey and Mill, 1978). However, hydrolysis is not the primary means of degradation for methyl chloride, although it usually is for methyl bromide. Neither is reduction to methane, which, although it is thermodynamically favored even at an Eh of +0.1 Volts, usually requires assistance from anaerobic microbes, which would not be found abundantly under these conditions. Thus, the microbially-mediated oxidation of methyl chloride to formaldehyde might be considered the important reaction (Vogel et al., 1987). If we assume that methyl chloride and methyl bromide are converted into formaldehyde by microbes at roughly the same rate, then the rate constant for this reaction for methyl chloride might lie between the hydrolysis rate constants for the two methyl halides. Using this type of logic, the hypothetical rate constants presented in Table 1 were generated.

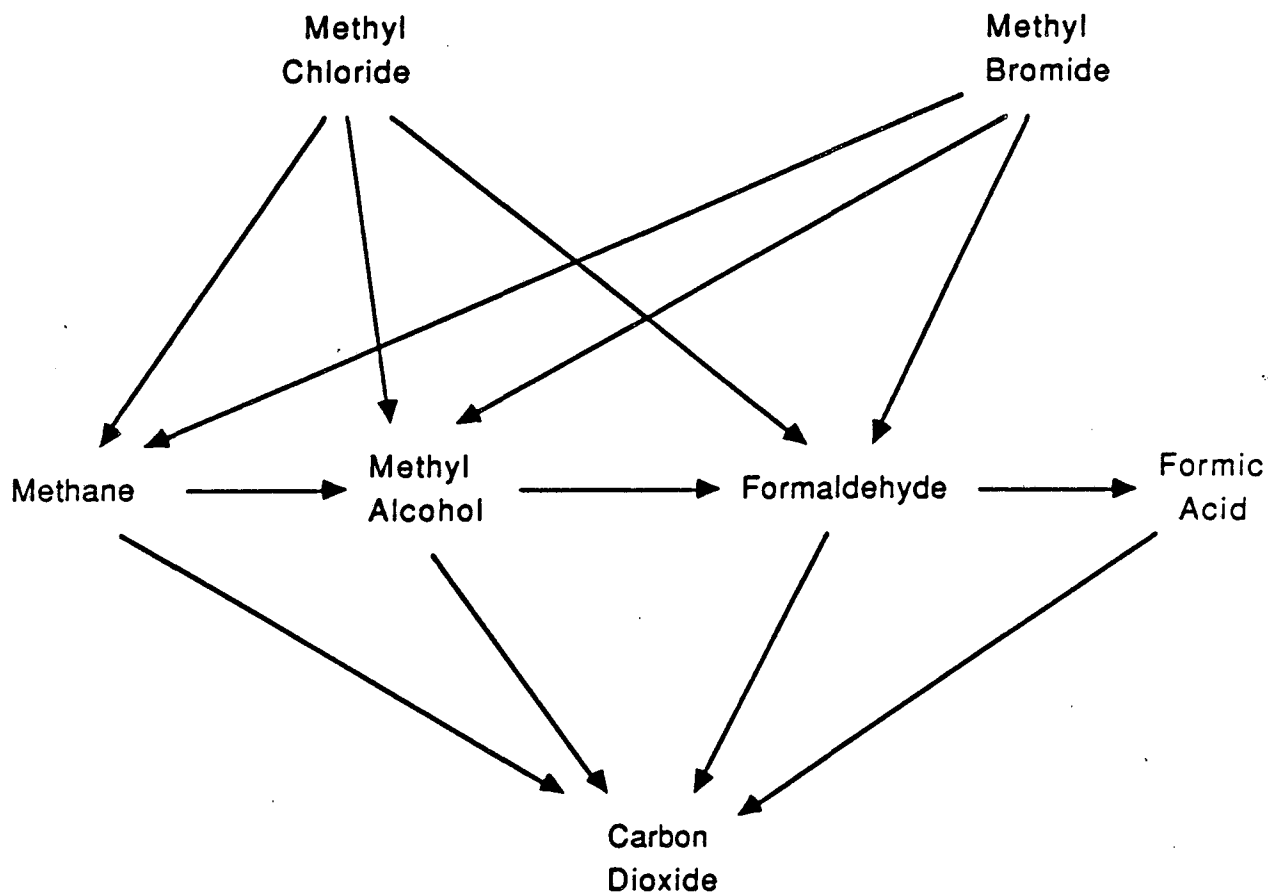


Figure 3. Possible pathways for the degradation of methyl chloride and methyl bromide under oxidizing conditions.

Table 1.

Degradation Reactions for Methyl Chloride and Methyl Bromide  
at pH = 7.0 and Eh = +0.1 Volts

Reaction*	Type	Half-life** (days)	$k_{\text{forward}}$ ( $\text{sec}^{-1}$ )
$\text{CH}_3\text{Cl} \rightarrow \text{CH}_4$	reduction	10000	$8.02 \times 10^{-10}$
$\text{CH}_3\text{Cl} \rightarrow \text{CH}_3\text{OH}$	hydrolysis	338	$2.37 \times 10^{-8}$
$\text{CH}_3\text{Cl} \rightarrow \text{HCHO}$	oxidation	100	$8.02 \times 10^{-8}$
$\text{CH}_3\text{Br} \rightarrow \text{CH}_4$	reduction	10000	$8.02 \times 10^{-10}$
$\text{CH}_3\text{Br} \rightarrow \text{CH}_3\text{OH}$	hydrolysis	20	$4.09 \times 10^{-7}$
$\text{CH}_3\text{Br} \rightarrow \text{HCHO}$	oxidation	100	$8.02 \times 10^{-8}$
$\text{CH}_3\text{OH} \rightarrow \text{CH}_4$	reduction	10000	$8.02 \times 10^{-10}$
$\text{CH}_3\text{OH} \rightarrow \text{HCHO}$	oxidation	100	$8.02 \times 10^{-8}$
$\text{HCHO} \rightarrow \text{HCOOH}$	oxidation	200	$4.01 \times 10^{-8}$
$\text{CH}_4 \rightarrow \text{CO}_2$	oxidation	10	$8.02 \times 10^{-7}$
$\text{CH}_3\text{OH} \rightarrow \text{CO}_2$	oxidation	100	$8.02 \times 10^{-8}$
$\text{HCHO} \rightarrow \text{CO}_2$	oxidation	100	$8.02 \times 10^{-8}$
$\text{HCOOH} \rightarrow \text{CO}_2$	oxidation	10	$8.02 \times 10^{-7}$

\* See Appendix A for the complete reactions, as well as their equilibrium constants.

\*\* Note that the kinetic data presented here, with the exception of the two hydrolysis reactions (Mabey and Mill, 1978), are completely artificial and are used for demonstration purposes only. Such data are not to be used in evaluating the fate of any of the species mentioned for any real contamination site.

As mentioned, methane is actually thermodynamically favored over  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$  even at this Eh. Methane should also form as a result of equilibration with methyl alcohol, as  $\text{CH}_4$  and  $\text{CH}_3\text{OH}$  will have nearly the same equilibrium concentrations under these conditions, although they will be extremely small. Nevertheless, from experience one would not often expect to find much methane produced under these relatively oxidizing conditions. Because of this, we suppress methane accumulation by specifying very slow rates of production and very rapid oxidation of methane to  $\text{CO}_2$ . Similarly, formic acid is not often mentioned as a common species in such situations, thus we accelerate its destruction by allowing it to oxidize to carbon dioxide rapidly as well. A "real-world" explanation for this might be the presence of microorganisms in the soil which are capable of metabolizing these substances.

Methyl bromide and methyl chloride, depicted in Figure 4, show simple exponential decay. This is because neither is being produced directly in any forward reactions, and the reverse reaction rates for the degradation reactions of the two are exceedingly small. In Figure 5, the secondary organic species show more complex behavior, however. The concentrations of methane and formic acid, and particularly methyl alcohol and formaldehyde, show a rapid increase initially as they are produced through degradation reactions. However, as the primary pollutant concentrations begin to fall off, the secondary organic species begin to be destroyed (i.e. oxidation to  $\text{CO}_2$ ) faster than they are produced, thus explaining their transient behavior as shown in the plot. The concentration of total aqueous  $\text{CO}_2$  rises steadily over time, as one would expect.

The free halogen ions,  $\text{Cl}^-$  and  $\text{Br}^-$ , show concentrations that do not vary significantly after 50 days or so (Figure 4). We believe this observation, along with the constant pH-Eh assumption, helps justify the reasoning that these reactions (see Appendix A) are approximately first-order in both directions, as pointed out in section 2.1.

### 3.2. Model Verification.

#### 3.2.1. Hypothetical Equilibration of Formic Acid with Carbon Dioxide.

A simple way to test whether or not the kinetics model is performing in a credible fashion is to allow the above reactions to continue to evolve until the entire system is at equilibrium and to compare the results at equilibrium with the calculated final equilibrium state of the system. However, a comparison of Figures 4 and 5 with Figures 1 and 2 shows that this may take a very long time to occur. A simpler test must therefore be devised. From Figure 2, we note that at Eh = +0.1 Volts, formic acid maintains an extremely small but finite concentration value in the presence of  $1.2 \times 10^{-3}$  moles/liter of total dissolved  $\text{CO}_2$ . In fact, from the reaction

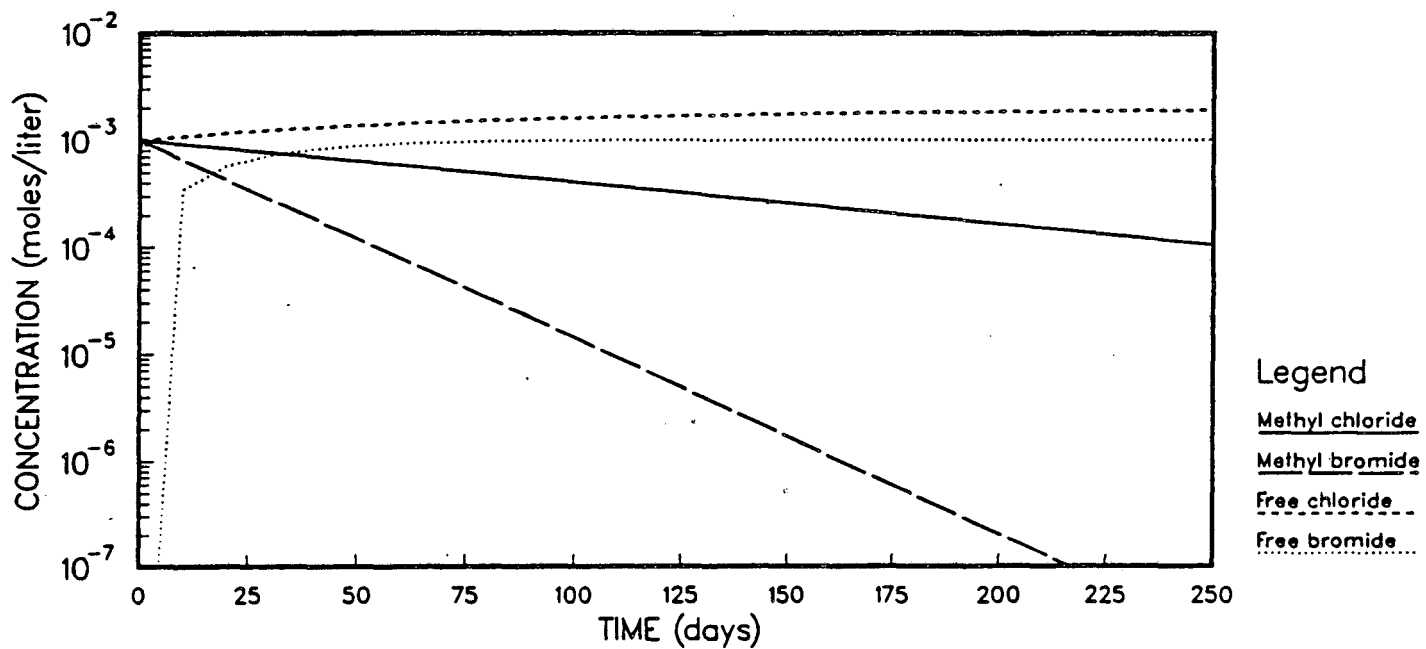


Figure 4. Batch simulation concentrations of methyl chloride and methyl bromide, along with the free halogen ions, as a function of time.



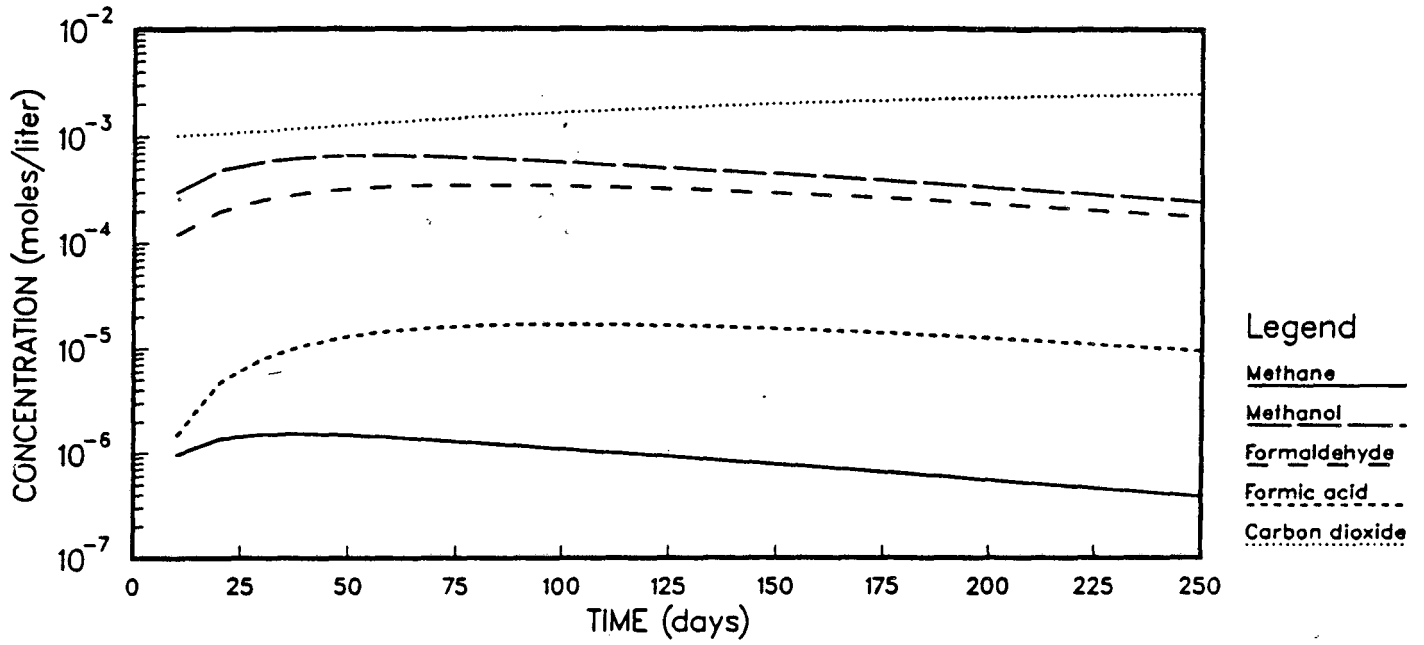
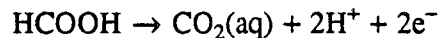


Figure 5. Batch simulation concentrations over time of the secondary species produced by the degradation of the two methyl halides.



we can write the mass action relationship

$$\frac{[\text{CO}_2(\text{aq})][\text{H}^+]^2[\text{e}^-]^2}{[\text{HCOOH}]} = 10^{-2.427}$$

From this expression, one can calculate that under these conditions,  $[\text{HCOOH}] = 1.868 \times 10^{-23}$  moles/liter. This is obviously an almost trivial number; it certainly could never be measured in the field. However, the model insists that this be a finite quantity in order that the mass action constraint to be satisfied.

Thus, if we take the kinetics simulator by itself, give it an initial pH of 7.0 and an Eh of +0.1 Volts, along with  $[\text{CO}_2] = 1.2 \times 10^{-3}$  moles/liter, all other species concentrations being zero, then this hypothetical equilibrium value for  $[\text{HCOOH}]$  should be eventually achieved. As seen from Figure 6, this is precisely what the model calculates. HCOOH-CO<sub>2</sub> equilibrium is achieved after about 100 days. The use of (10) from section 2.2 to calculate the  $\lambda$ -parameter was very successful; the plot shows a smooth approach to the equilibrium value. No oscillations occur, and the model does not overestimate or underestimate the equilibrium value to any measurable degree. This gives us confidence that the kinetics algorithm in KINETRAN is functioning correctly.

### 3.2.2. Verification of the Transport Model.

Before the complete reactive transport problem was run attempted, a comparison of the performance of the transport module used in KINETRAN against a modified version of the well-established chemical/heat transport program TRUMP (Edwards, 1972) was performed. Using the initial conditions described above, both programs simulated the non-reactive transport of methyl chloride. Results from the two models, shown compared in Figure 7, indicate excellent agreement between the models.

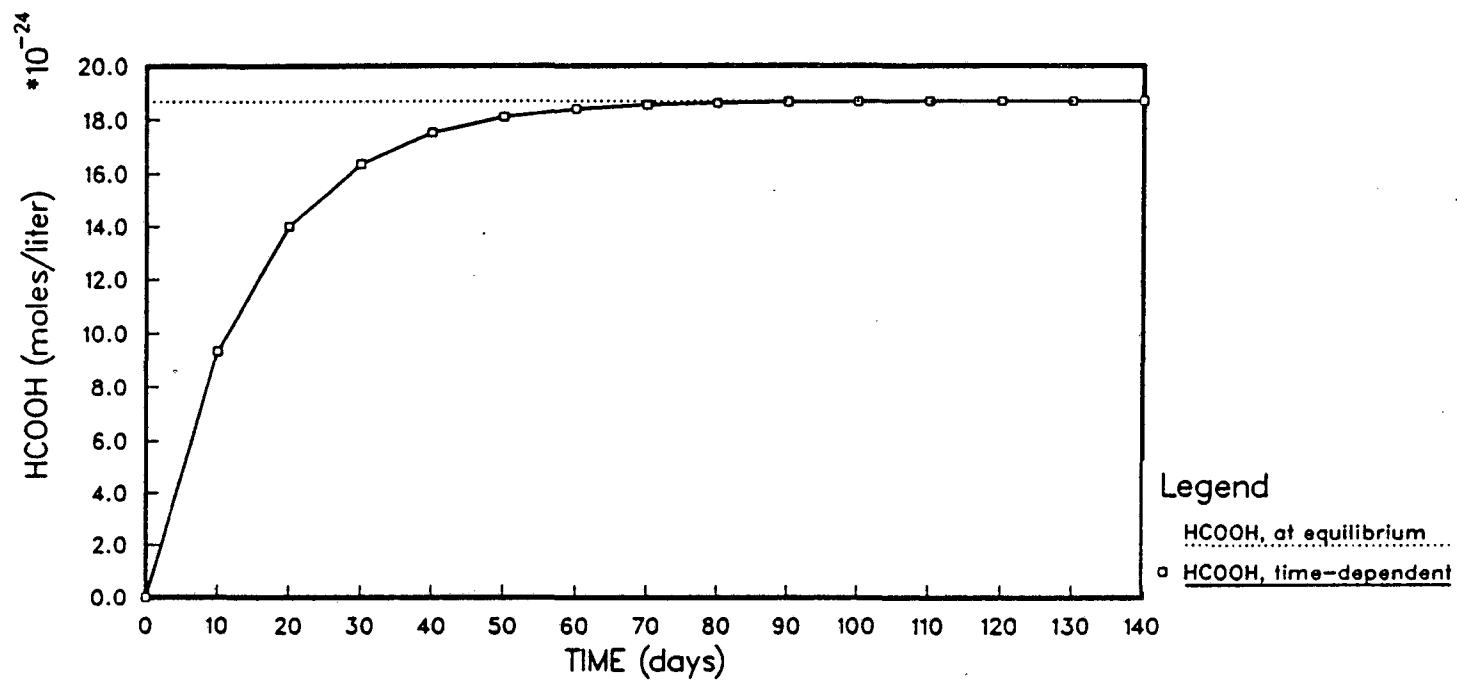


Figure 6. Hypothetical equilibration of formic acid with carbon dioxide over time.

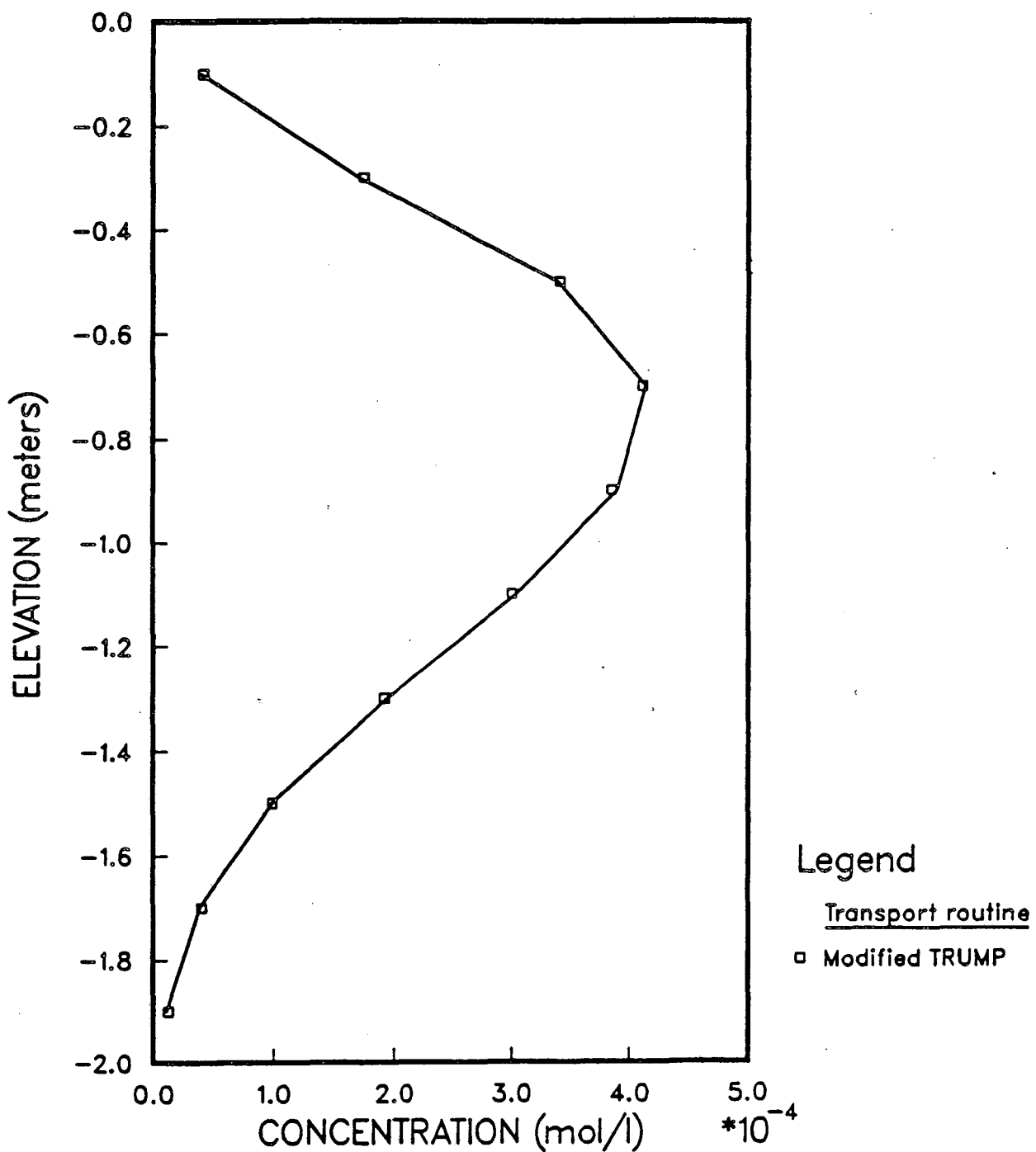


Figure 7. Comparison of the transport module in KINETRAN with the results from the chemical/heat transport program TRUMP.

### 3.3. Combined Transport and Transformation Effects.

#### 3.3.1. Problem Definition.

We now apply the whole KINETRAN model to a hypothetical problem involving the simultaneous transport and chemical transformation of two halogenated hydrocarbons through a one-dimensional soil column. The species considered for this problem are the same set that we have used as an example throughout this paper, as listed in section 2.3.1.

The physical configuration of the problem is depicted in Figure 8. A one-dimensional soil column 2 meters in depth with a cross-sectional area of 1 m<sup>2</sup> is divided into 10 equal volume elements. A constant, uniform fluid flux, representing infiltrating rainwater, flows toward the bottom at the rate of 0.508 meters/year, or, volumetrically,  $1.611 \times 10^{-8}$  meters<sup>3</sup>/second. The column consists of a homogeneous material with a porosity of 0.25, a neutral pH of 7.0, and a mildly oxidizing Eh of +0.1 Volts. The effective diffusion coefficients for all species are assumed to be equal to  $1 \times 10^{-10}$  meters<sup>2</sup>/second and the longitudinal dispersivities 0.1 meter. Adsorption is neglected for this simulation so  $K_d = 0$  for all species. The column is assumed to be fully saturated with fluid at all times. The column is under isothermal conditions at 25 ° C. A constant time step of 10 days is used for the simulation, with the total simulation time set at 100 days.

Initially, [CH<sub>3</sub>Cl] and [CH<sub>3</sub>Br] occur at equal concentrations of 10<sup>-3</sup> moles/liter in the uppermost two volume elements of the column, representing a spill. Throughout the column, and in the infiltrating rainwater entering the top of the column, background total [CO<sub>2</sub>(aq)] is 10<sup>-3</sup> moles/liter, [Cl<sup>-</sup>] is 10<sup>-3</sup> moles/liter, and [Br<sup>-</sup>] is 10<sup>-10</sup> moles/liter. All other species considered, throughout the entire column, occur at zero concentrations.

#### 3.3.2. Simulation Results.

The concentration profiles of methyl chloride after 20 days and 100 days are shown in Figure 9 and 10, respectively. Also shown for comparison are results pertaining to transport without transformation. Figure 9 shows that the two profiles are fairly similar after 20 days, as not enough time has elapsed for the material to degrade significantly. After 100 days, however, much of the methyl chloride has been transformed into other species. The profile for the reactive case shows a front that is much less sharp than for the non-reactive case. This is reasonable, since the material will degrade more quickly where it is more abundant (near the 0.8 meter depth mark). Incidentally, integration under the reactive transport profile curves shows that the total amount of CH<sub>3</sub>Cl present after a given time is consistent with that predicted in the batch simulation. This is important as it indicates that mass is conserved through the

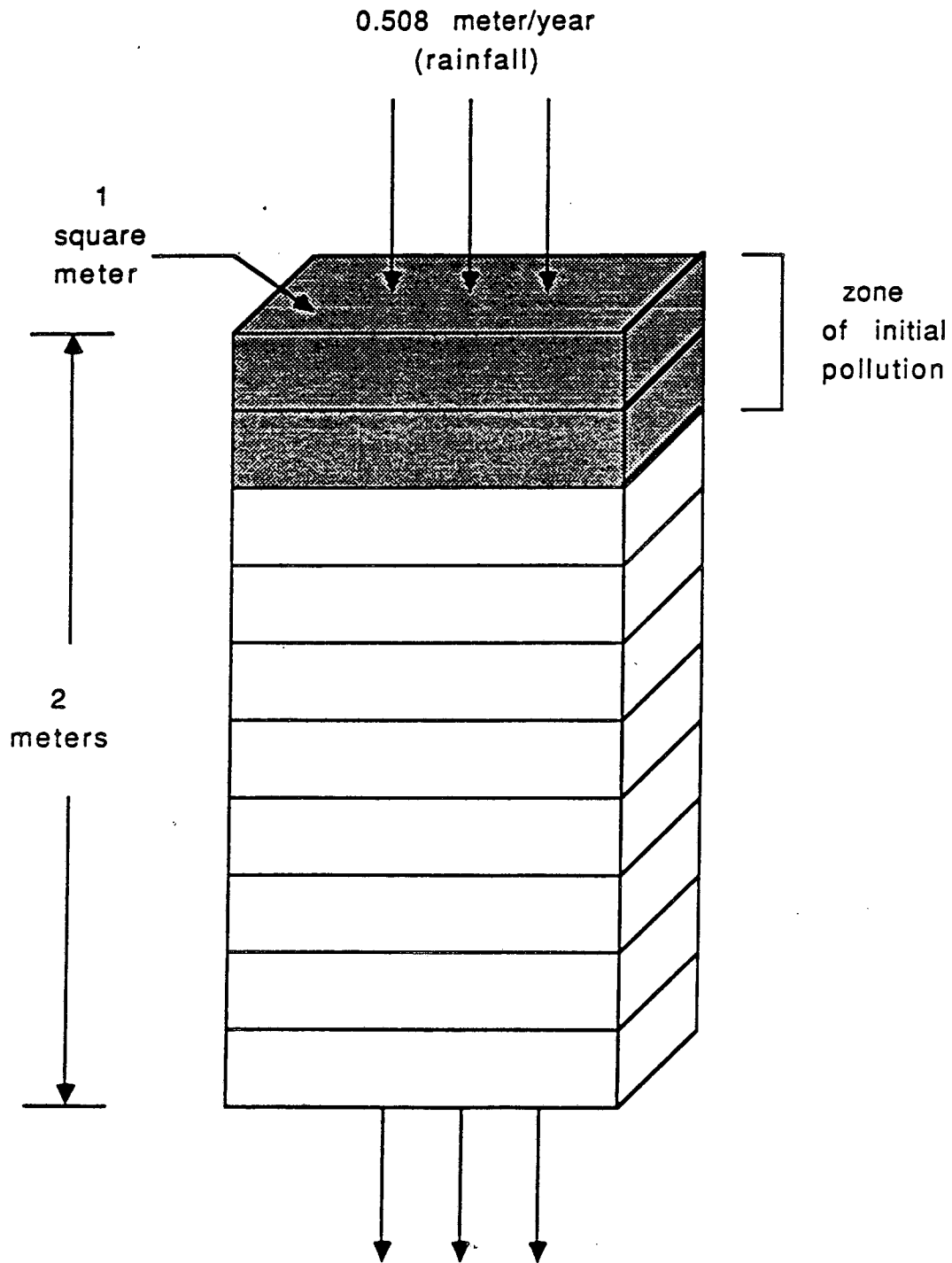


Figure 8. Physical configuration for the hypothetical soil or rock column used for the example simulation.

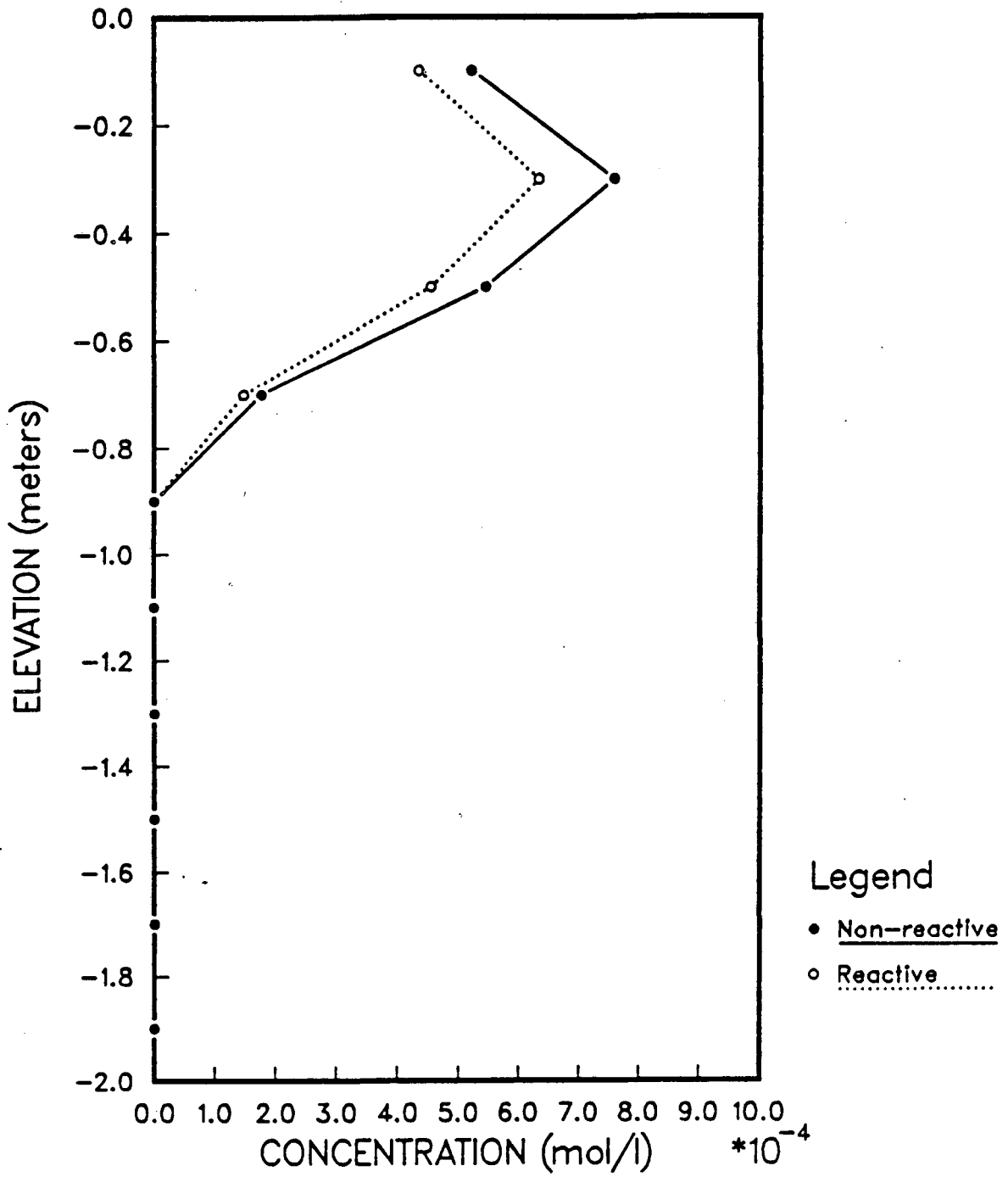


Figure 9. Concentration profiles of methyl chloride in the soil column after 20 days, showing the reactive and non-reactive cases.

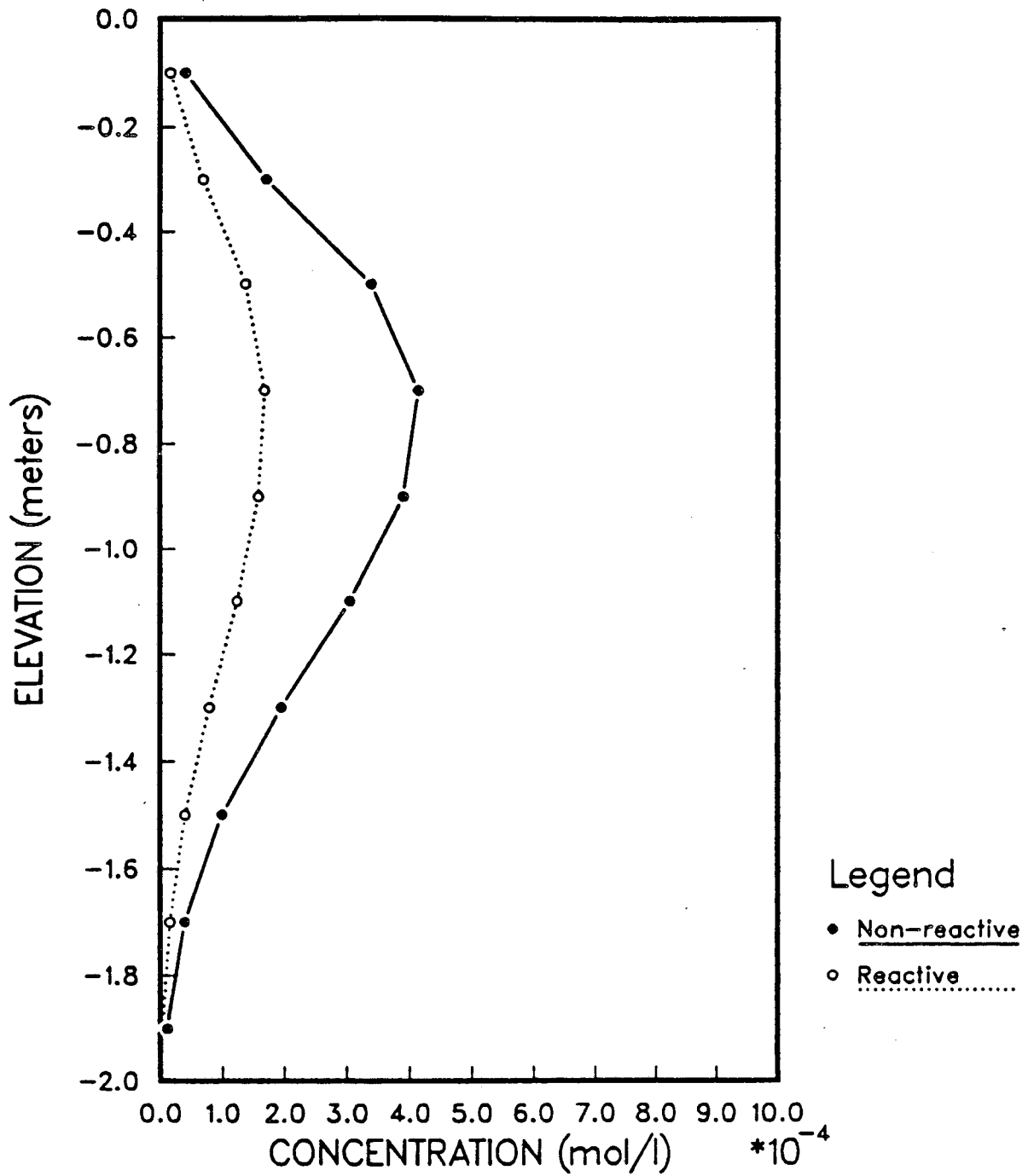


Figure 10. Concentration profiles of methyl chloride in the soil column after 100 days, showing reactive and non-reactive cases.



kinetics-transport coupling in the program, a necessary condition for internal mathematical consistency.

The profiles for methyl bromide are shown in Figures 11 and 12. It behaves similarly, although it degrades much faster, being significantly transformed after just 20 days. For the 100-day profile shown in Figure 12, a log scale had to be used for the concentration because the reactive and non-reactive cases could not be plotted together effectively with a linear scale.

Reactive transport profiles for the secondary, or transient organic species are shown in Figures 13 and 14. Clearly, methyl alcohol and formaldehyde are the most important primary degradation products for these two methyl halides, which is consistent with what was found in the literature (Mabey and Mill, 1978 and Vogel et al., 1987). Figure 14 shows that after 100 days, the level of CO<sub>2</sub> near the center of the column has risen measurably above background levels, which one would expect as the hydrocarbon species are progressively oxidized.

### 3.3.3. Reactive Hydrocarbon Transport in the Presence of a Reducing Layer.

As an additional part of the study, we modified the problem definition so that a layer of reducing material was introduced in the soil matrix below 0.8 meters depth. The same initial conditions as described earlier were used, except that the Eh in nodes 5 through 10 was set to -0.3 Volts. The reaction kinetics within this zone were also modified (see Table 2). Instead of CO<sub>2</sub>(aq) being present in background concentrations, dissolved methane was present instead, at the same concentration. The results of this simulation are depicted in Figures 15 and 16.

As seen from Figure 15, after 20 days methyl alcohol and formaldehyde have formed in the oxidizing zone, but have not yet reached the reducing layer. A generally sharp redox front is maintained at the 0.8 meter depth mark, although a small amount of CO<sub>2</sub> can be detected in the reducing zone. Because of advection and dispersion, it has been transported into this zone slightly faster than it can be reduced. Methane, on the other hand, must travel upstream in order to infiltrate the oxidizing zone, thus it is assisted only by diffusive processes, and is opposed by advection. As a result, methane is transported upstream at a rate slower than its oxidation rate in the oxidizing zone, so we do not see the corresponding "tongue" of methane in this zone the way we see it for CO<sub>2</sub> in the reducing zone.

It is seen from Figure 16 that the methane and carbon dioxide profiles after 100 days are similar to those at 20 days, except that they show a greater-than-background concentration where the peak amounts of infiltrating pollutants occur, as shown in Figures 10 and 12. The methyl alcohol profile closely resembles the profile for the homogeneous case shown in Figure 14, thus the reducing zone seems to have no effect on it. This is because alcohol is produced

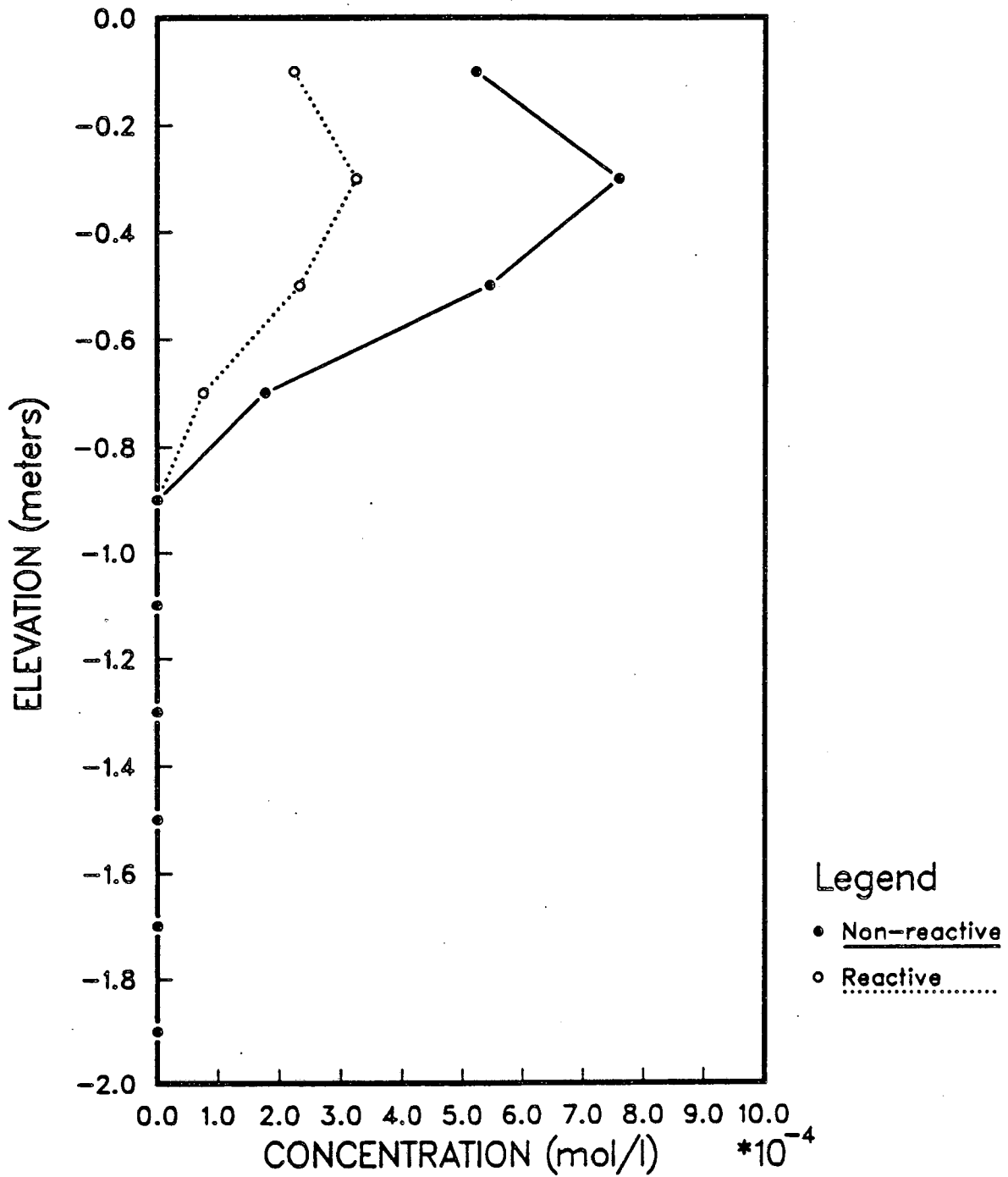


Figure 11. Concentration profiles for methyl bromide in the column after 20 days for reactive and non-reactive cases.

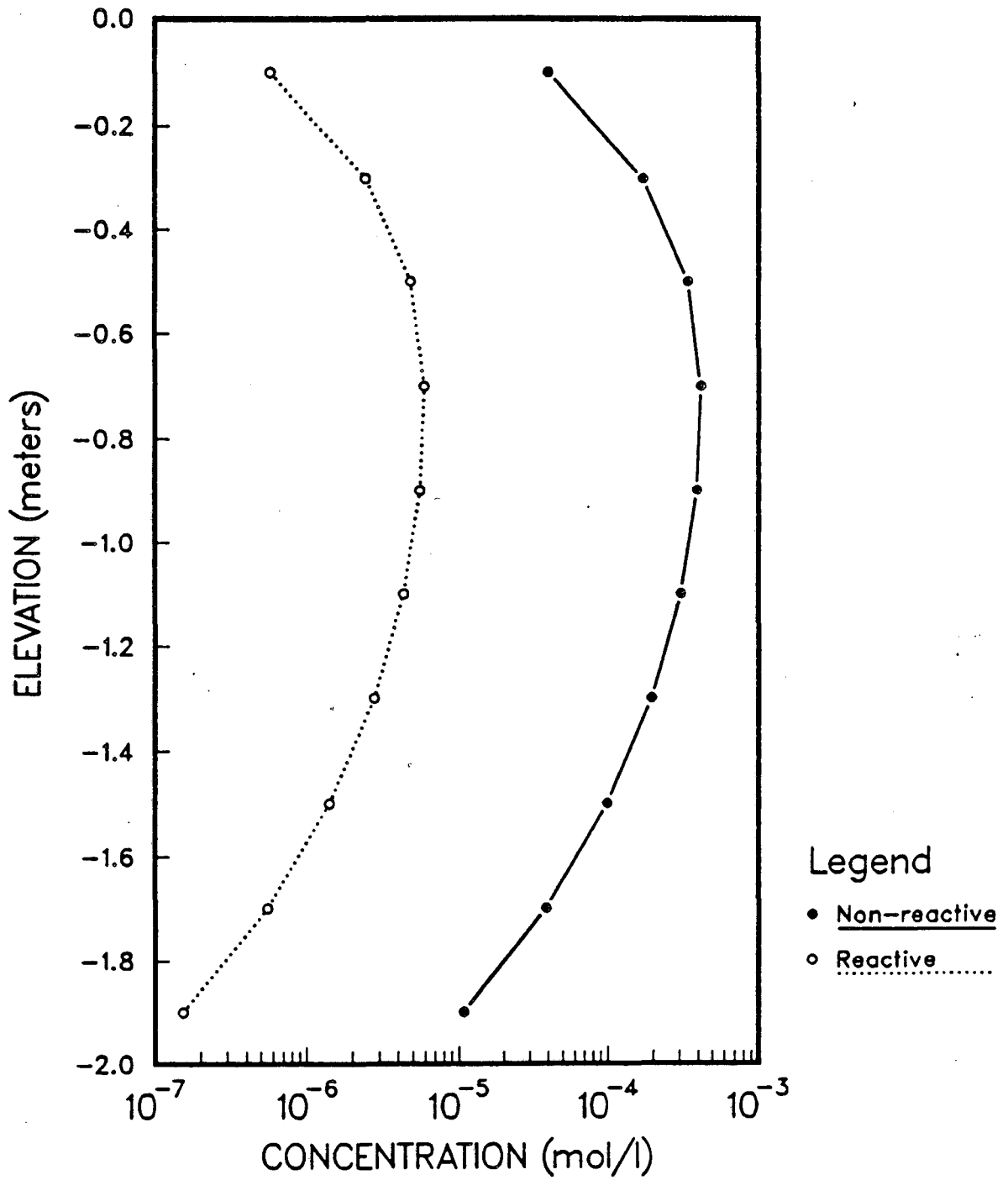


Figure 12. Concentration profiles for methyl bromide in the column after 100 days for reactive and non-reactive cases.

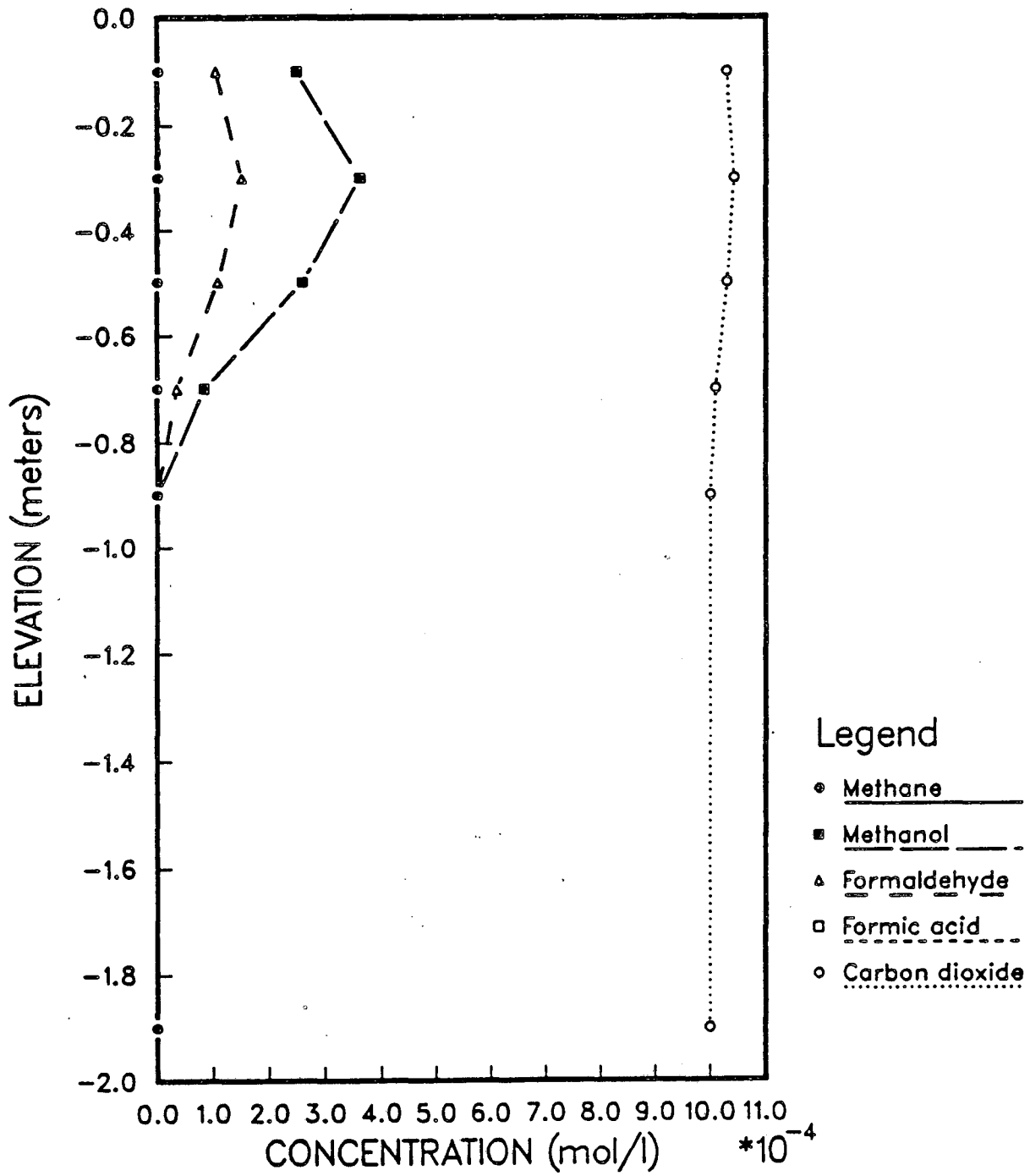


Figure 13. Reactive transport profiles for the secondary species in the soil column after 20 days.

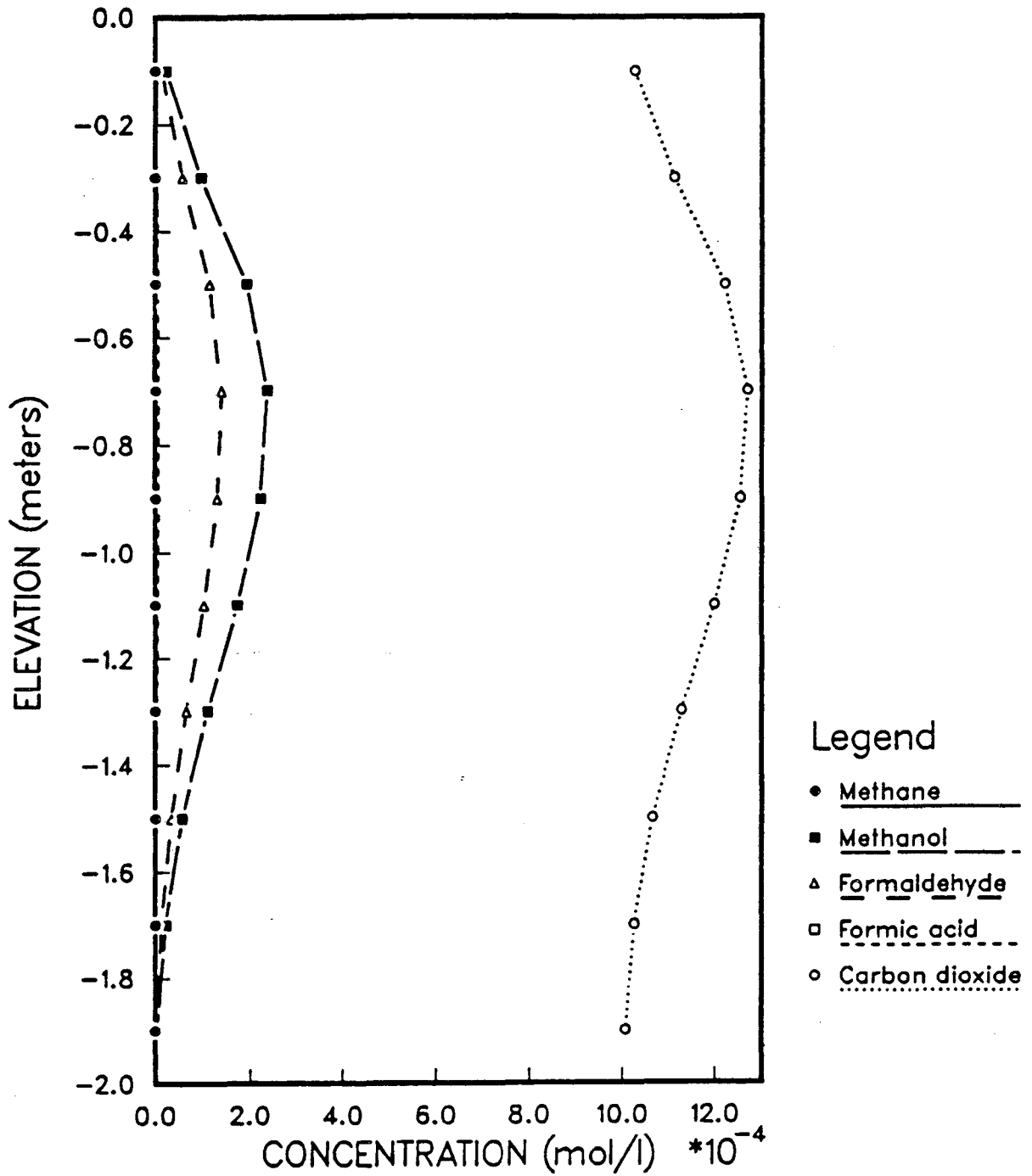


Figure 14. Reactive transport profiles for the secondary species after 100 days have elapsed.

Table 2.

**Degradation Reactions for Methyl Chloride and Methyl Bromide  
at pH = 7.0 and Eh = -0.3 Volts**

Reaction*	Type	Half-life** (days)	k <sub>forward</sub> (sec <sup>-1</sup> )
CH <sub>3</sub> Cl → CH <sub>4</sub>	reduction	100	8.02 × 10 <sup>-8</sup>
CH <sub>3</sub> Cl → CH <sub>3</sub> OH	hydrolysis	338	2.37 × 10 <sup>-8</sup>
CH <sub>3</sub> Cl → HCHO	oxidation	10000	8.02 × 10 <sup>-10</sup>
CH <sub>3</sub> Br → CH <sub>4</sub>	reduction	100	8.02 × 10 <sup>-8</sup>
CH <sub>3</sub> Br → CH <sub>3</sub> OH	hydrolysis	20	4.09 × 10 <sup>-7</sup>
CH <sub>3</sub> Br → HCHO	oxidation	10000	8.02 × 10 <sup>-10</sup>
CH <sub>3</sub> OH → CH <sub>4</sub>	reduction	100	8.02 × 10 <sup>-8</sup>
HCHO → CH <sub>3</sub> OH	reduction	100	8.02 × 10 <sup>-8</sup>
HCHO → HCOOH	oxidation	10000	4.01 × 10 <sup>-10</sup>
CO <sub>2</sub> → CH <sub>4</sub>	reduction	10	8.02 × 10 <sup>-7</sup>
CH <sub>3</sub> OH → CO <sub>2</sub>	oxidation	10000	8.02 × 10 <sup>-10</sup>
HCHO → CO <sub>2</sub>	oxidation	10000	8.02 × 10 <sup>-10</sup>
HCOOH → CO <sub>2</sub>	oxidation	10000	8.02 × 10 <sup>-10</sup>

\* See Appendix A for the complete reactions, as well as their equilibrium constants.

\*\* Note that the kinetic data presented here, with the exception of the two hydrolysis reactions (Mabey and Mill, 1978), are completely artificial and are used for demonstration purposes only. Such data are not to be used in evaluating the fate of any of the species mentioned for any real contamination site.

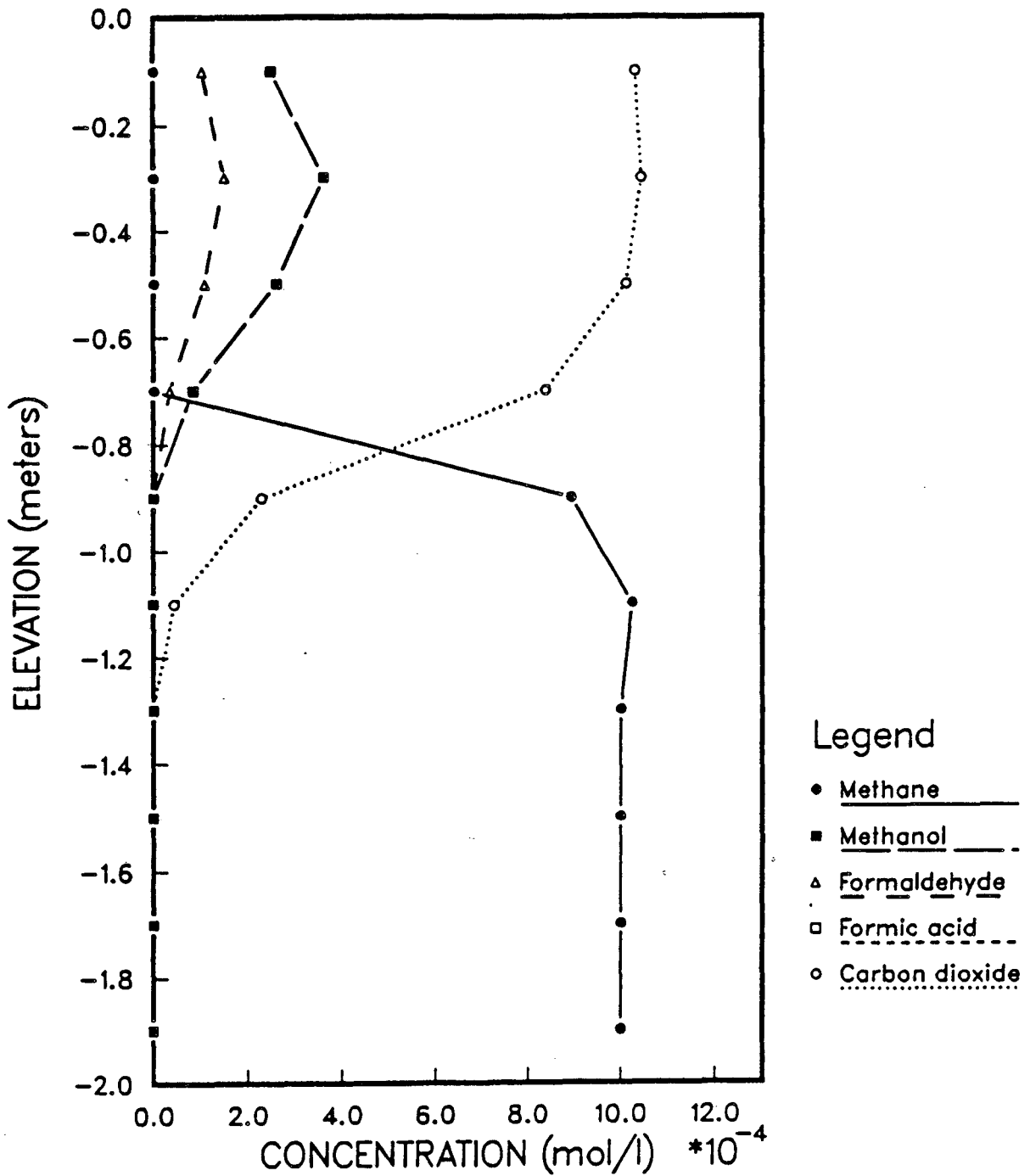


Figure 15. Reactive transport profiles of the degradation products of the methyl halides in the presence of a reducing layer; t = 20 days.

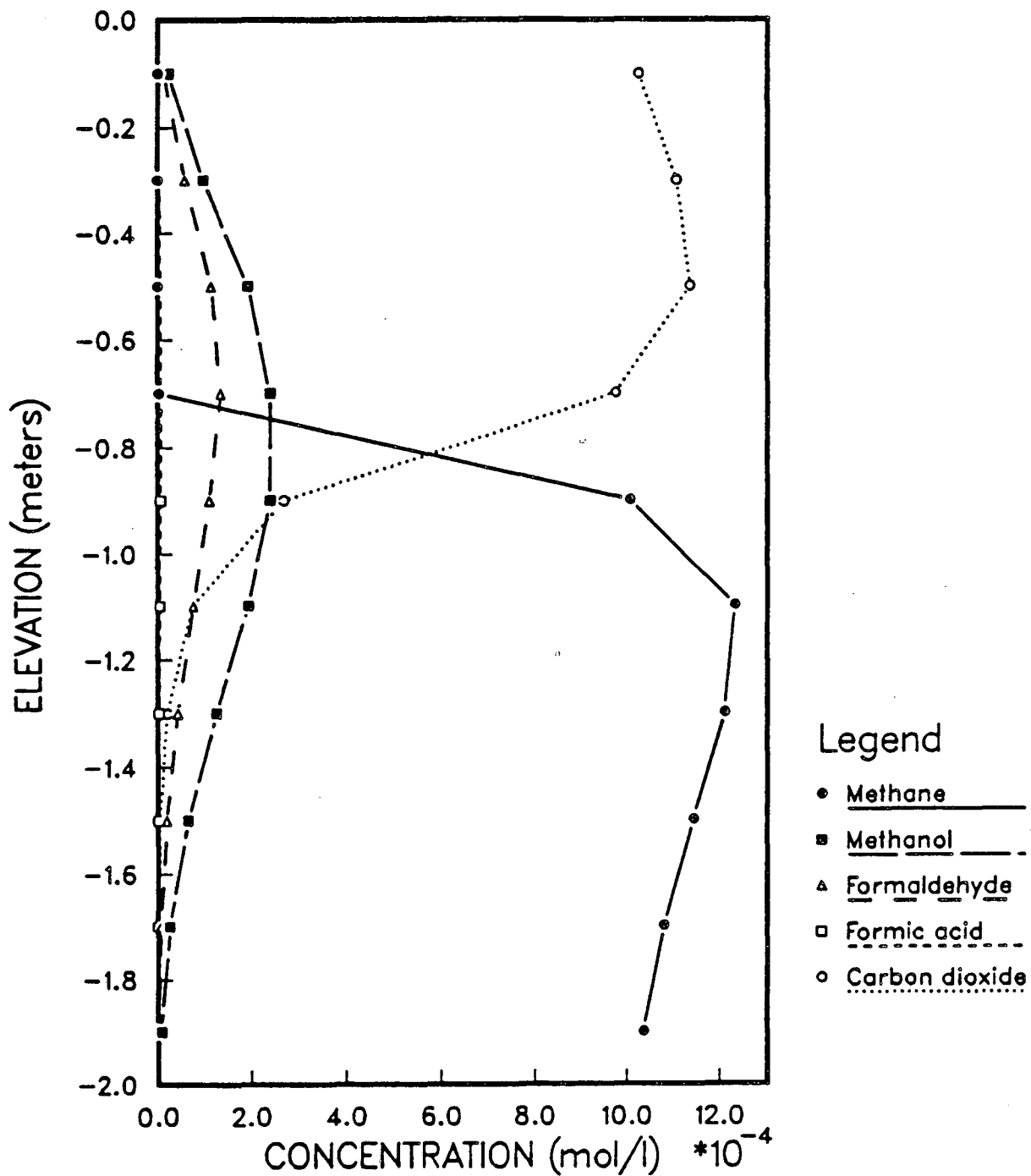


Figure 16. Reactive transport profiles of the secondary species in the soil column containing a reducing layer;  $t = 100$  days.



in this system primarily by the hydrolysis of the two methyl halides, and these reactions do not involve electron transfer, hence are independent of the prevailing redox state. Formaldehyde, on the other hand, seems to show a slight asymmetry in its concentration profile. It is likely that this results from formaldehyde being generated mainly in the oxidizing zone, so the HCHO present in the reducing zone has not been produced there. Rather, it was transported there from the oxidizing zone above and has not yet had enough time to degrade into other species.

It must be emphasized that the results described above are derived strictly from the simulation of a hypothetical scenario which is not based on any particular contamination problem that may exist in the field. It would certainly be encouraging to find quantitative data in the literature that would be useful for validating the above simulations as good approximations of the real world. However, such data are quite scarce, and often contain too much uncertainty about the physical and chemical characteristics of the systems they describe. Thus, for now, we must be content with attempting to verify the model by showing that it produces credible, internally consistent results.

#### 4. CONCLUSIONS

A numerical model, KINETRAN, is presented in this study as an attempt to solve reactive transport problems involving chemical transformations of aqueous species which are controlled by reversible, first-order kinetics. Given a hypothetical problem, such as the one we present, the model is shown capable of producing credible results that are consistent with the input data and with expected patterns of spatial and temporal distribution of chemical species. The model simulates the appearance and decline of various transient species, which would not be explained properly using a purely equilibrium model. In fact, in many contamination scenarios, such transient species may be of paramount environmental concern.

We believe that one of the potentially important uses for programs such as this will be to quantify the reaction kinetics of real systems by calibration exercises if they are not well known beforehand. Such information would prove to be invaluable for further experimentation.

It is important to emphasize that KINETRAN is only a tentative, *prototype model*. It makes many simplifying assumptions; additional improvements will be required in order to simulate real systems. Nonetheless, our limited purpose here is to show that the model serves as a nucleus upon which to build further development that will eventually lead to a far more sophisticated simulator for field applications.

The model will be developed further on several fronts. The most important of these will be an attempt to partially validate the model by applying it to a well-characterized field site containing halogenated hydrocarbons. Our hope is that the model will be able to simulate the behavior of these compounds in groundwater with reasonable reliability. In addition, we will modify the kinetics algorithm so that it will be able to handle reactions that are not necessarily first-order. Finally, we plan to further increase the flexibility of the model by allowing for mass balance corrections for carbon due to its uptake by microorganisms, and by modifying the transport subroutine so that transient advective fluid flow may be taken into account.

#### ACKNOWLEDGMENTS

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## Appendix A

### Chemical Reactions Considered in the Sample Problem.

We present here the complete set of chemical reactions that were used in the demonstration problems in this paper, along with the corresponding equilibrium constants. The values for the various  $K_{eq}$  were determined from the Gibbs free energies of formation of the species in the aqueous state. In cases where these were unavailable, the gaseous state  $\Delta G_f^0$  values were used, and adjusted for the aqueous state using the formula,

$$\Delta G_f^0(aq) = \Delta G_f^0(g) + RT \ln H$$

where  $H$  is the value of Henry's constant for the particular species.

These data were collected from several sources, and there is almost certainly some degree of error within our thermodynamic data base. This is often a problem in trying to accurately determine the equilibrium chemistry of complex systems in general. However, we do not believe that this is serious enough to have a major impact on our simulation results. As our study has shown, the systems we consider are generally far from equilibrium anyway, and most of the reactions considered remain dominant in one direction. As a result, uncertainties in the values for the reverse direction kinetic constants, where errors in the  $K_{eq}$  values would be manifested, are probably not critical to the outcome of the simulation.

Table A.1 shows all of the reactions considered in this work. These include reactions that are controlled by kinetics, such as those depicted in Figure 3, as well as reactions that are used for equilibration. Note that some of the equilibration reactions, such as  $CH_3Cl \rightarrow CO_2$ , are not considered to actually take place in the system, at least directly.

Table A.1.

Reaction	log K <sub>eq</sub>
$\text{CH}_3\text{Cl} + \text{H}^+ + 2\text{e}^- \rightarrow \text{CH}_4 + \text{Cl}^-$	20.01
$\text{CH}_3\text{Cl} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + \text{H}^+ + \text{Cl}^-$	3.154
$\text{CH}_3\text{Cl} + \text{H}_2\text{O} \rightarrow \text{HCHO} + 3\text{H}^+ + \text{Cl}^- + 2\text{e}^-$	-4.852
$\text{CH}_3\text{Cl} + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{Cl}^- + 7\text{H}^+ + 6\text{e}^-$	-1.465
$\text{CH}_3\text{Br} + \text{H}^+ + 2\text{e}^- \rightarrow \text{CH}_4 + \text{Br}^-$	22.41
$\text{CH}_3\text{Br} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + \text{H}^+ + \text{Br}^-$	5.557
$\text{CH}_3\text{Br} + \text{H}_2\text{O} \rightarrow \text{HCHO} + 3\text{H}^+ + \text{Br}^- + 2\text{e}^-$	-2.449
$\text{CH}_3\text{Br} + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{Br}^- + 7\text{H}^+ + 6\text{e}^-$	-0.938
$\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 8\text{H}^+ + 8\text{e}^-$	-21.47
$\text{CH}_3\text{OH} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CH}_4 + \text{H}_2\text{O}$	16.855
$\text{CH}_3\text{OH} \rightarrow \text{HCHO} + 2\text{H}^+ + 2\text{e}^-$	-8.006
$\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^-$	-4.619
$\text{HCHO} + \text{H}_2\text{O} \rightarrow \text{HCOOH} + 2\text{H}^+ + 2\text{e}^-$	0.96
$\text{HCHO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}^+ + 4\text{e}^-$	3.387
$\text{HCOOH} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$	2.427
$\text{H}^+ + \text{HCO}_3^- \rightarrow \text{H}_2\text{CO}_3$	6.37
$2\text{H}^+ + \text{CO}_3^{2-} \rightarrow \text{H}_2\text{CO}_3$	16.7
$\text{HCOO}^- + \text{H}^+ \rightarrow \text{HCOOH}$	3.739

Sources: Garrels and Christ (1965), Wagman et al. (1968), MacKay and Shin (1981)

## Appendix B

### The Logic Structure of the KINETRAN Program.

#### 1. The Algorithm.

A schematic flow chart of the logic structure of KINETRAN is shown in Figure B.1. The program consists of essentially two primary modules, a transport module and the kinetics module, which is itself divided into smaller units. The program is designed so that a simple switch can be used to completely uncouple the entire kinetics module, reducing the program to strictly a non-reactive chemical transport model. This option is useful in comparing the concentration profiles of a given species in the reactive case and the non-reactive case.

At present, KINETRAN is being converted into standardized FORTRAN IV and is being coupled with a more sophisticated transport code for use on a mainframe computer. This will allow the program to handle larger, more complex problems. The original program was written in the BASIC language and was designed to be run on a desktop personal computer. Because of this, in describing the program algorithm, we will discuss only the overall logic of the program and will deliberately avoid reference to any particular programming language.

#### 1.1. The Input Module.

The input module is entered only once at the start of the program. Here, all of the critical information describing the physical and chemical characteristics of the system are input. The program is designed to handle both physical and/or chemical heterogeneities, so the user must specify how many different materials are present in the system, and then define separate diffusion coefficients, dispersivities, and distribution coefficients (per species), as well as material density, porosity, pH, Eh, and the kinetic coefficients for the dominant reactions (see section 2.1) for each material. Data regarding the discretization of the system is input, and an indexing system assigns the correct material number to the correct volume elements. At present, the steady-state advective fluxes between the volume elements must be user-specified. If these are not well known beforehand, a groundwater fluid flow model can be used to determine the final steady-state fluid flow if fluid potentials are known initially. Finally, initial concentrations of the species present in the system are input for each node.

In the prototype model used for this study, the chemical reactions that take place are "hard-coded" into the program with regard to thermodynamic relationships, setting up the

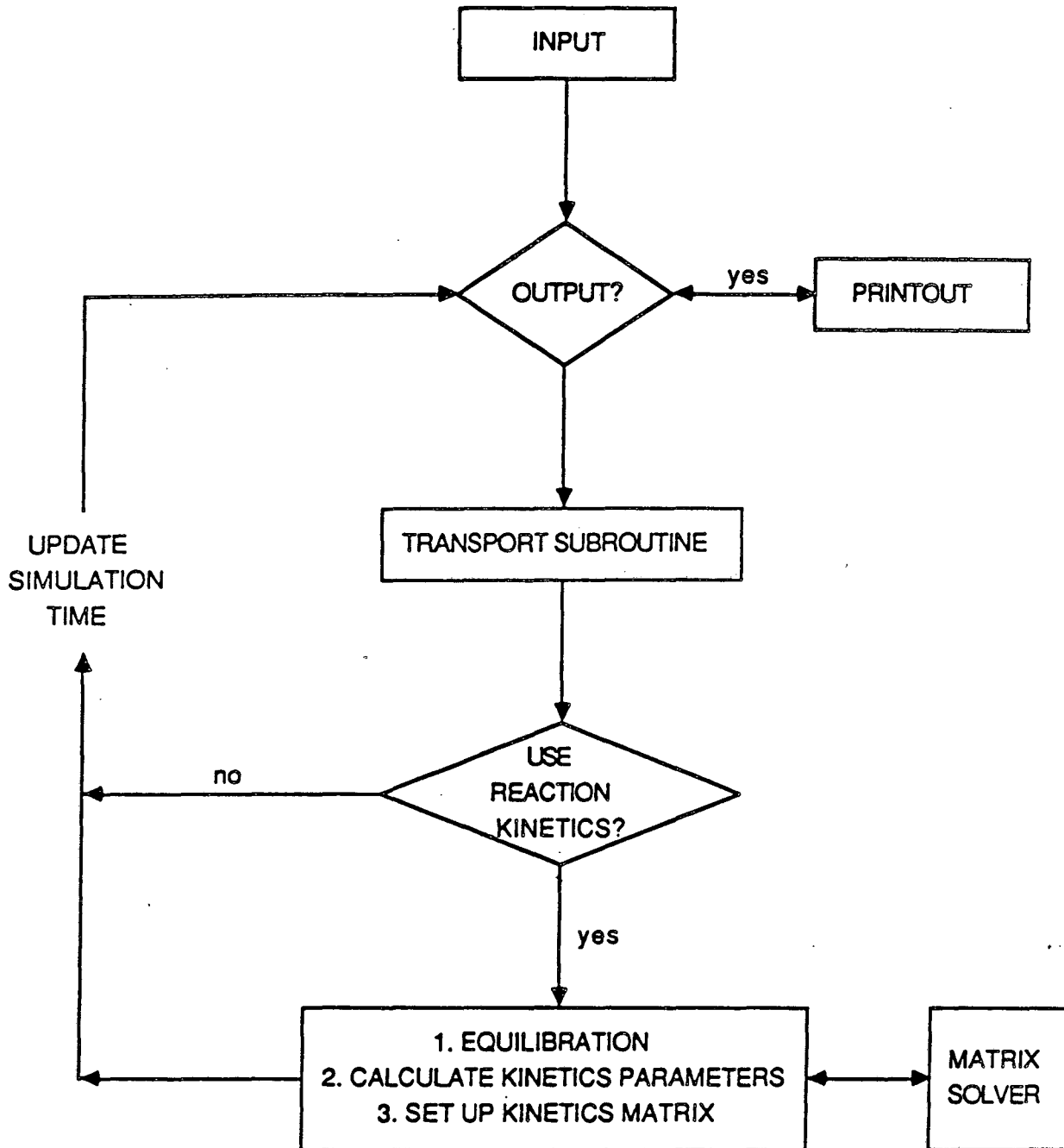


Figure B.1. The logic structure of KINETRAN.

kinetics matrix, etc. This makes the program somewhat cumbersome to use if one is considering a wide variety of problems, so we intend to modify it to allow for more general problem formulation in the future.

In addition to the physical and chemical characterization of the system, overall simulation controls, such as time step size, printout times, and termination criteria are also input from within this module.

### 1.2. The Transport Module.

The chemical transport module simply solves Equation (12) for  $\Delta c_i$ . This is done every time step, volume element by volume element.  $c_i$  is then updated for every node. This process must be repeated for every species  $i$  in the system. When this entire process is finished, the kinetics module is called, if required, to solve for  $\Delta c_i$  for all  $i$  as a result of chemical reactions separately for every node. Then the problem time is incremented by  $\Delta t$ , and the entire scheme is repeated.

The present transport routine is somewhat limited in that it cannot handle transient advective fluid flow which results from changing fluid potentials. By replacing this module with a more sophisticated model capable of handling such features, the utility and flexibility of KINETRAN will be greatly increased.

### 1.3. The Kinetics Module.

The module which handles the reaction kinetics between the various species present simply follows the logic outlined in this paper.  $\Delta c_i$  is calculated for every species, within every volume element in the system. This is done by looking at each of the volume elements separately, solving for the species concentrations within each as if they were separate batch systems.

The final equilibrium state of all of the species within given volume element is calculated first. These values are stored so that the program can then calculate the kinetic coefficients of the reverse reactions. These constants are then indexed according to the reaction they are associated with and the direction. Using Equation (10), the  $\lambda$ -parameters are then determined and indexed accordingly.

Next, the matrix of equations is set up using the newly determined parameters. The matrix is solved using standard Gaussian elimination with pivoting. The species concentrations for the particular volume element are then updated (hence the source term in the transport equation), and the process is repeated for the next volume element until the entire domain has been covered.

Following this, the simulation time is updated and a check is made to see if output is to be produced for the just completed time step. If it is, any instantaneous reactions, such as the speciation of  $\text{CO}_2$  into carbonate and bicarbonate ions, are calculated using the iterative technique used earlier. Output is then produced, and a new cycle is initiated.



## List of Symbols, Kinetics Equations

Symbol	Definition
$A_{i,m}$	Element in the implicit kinetics matrix
$[A_0]$	Initial concentration of A at start of time step
$B_i$	Element in the explicit kinetics matrix
$B'_{n(i,m)}$	Factor used in calculation of $B_i$
$c_i$	Concentration of species $i$
$c_i^0$	Initial concentration of species $i$
$c_{m,j}^0$	Initial concentration of species $m$ in reaction $j$
$c_{m,j'}^0$	Initial concentration of species $m$ in reaction $j'$
$e^-$	The hypothetical aqueous electron
Eh	Electrical potential with reference to the standard hydrogen electrode
F	Faraday constant
$[i]$	Concentration/activity of any species $i$
$[i]^*$	Virtual concentration/activity of species $i$
$J_p$	Number of reactions in which a given species is produced
$J_r$	Number of reactions in which a given species is destroyed
$K_{eq}$	Thermodynamic equilibrium constant
$k_1$	Kinetic coefficient for a given forward reaction
$k_2$	Kinetic coefficient for a given reverse reaction
$k_{j,f}$	Kinetic coefficient for reaction $j$ , forward direction
$k_{j,r}$	Kinetic coefficient for reaction $j$ , reverse direction

$k_{n(i,m),d}$	Kinetic coefficient for reaction $n$ , direction $d$ , between $i$ and $m$
$N$	Total number of reaction said to occur in system
$pE$	Negative logarithm of the hypothetical aqueous electron concentration
$pH$	Negative logarithm of the hydrogen ion concentration
$s_i$	Species $i$ , as written in a reaction equation
$s_{m,j}$	Species $m$ produced in reaction $j$
$s_{m,j'}$	Species $m$ destroyed in reaction $j'$
$x$	Total concentration of a given component prior to normalization
$\Delta c_i$	Change in concentration of $i$ due to transformation
$\Delta c_{m,j}$	Change in concentration of $m$ in reaction $j$
$\Delta c_{m,j'}$	Change in concentration of $m$ in reaction $j'$
$\Delta t$	Simulation time increment
$\lambda$	Time-averaging coefficient for aqueous species concentration
$\lambda_{j,f}$	Time-averaging coefficient for reaction $j$ , forward direction
$\lambda_{j,r}$	Time-averaging coefficient for reaction $j$ , reverse direction
$\lambda_{n(i,m),d}$	Time-averaging coefficient for reaction $n$ , direction $d$ , involving $i$ and $m$
$\mu_{i,j}$	Stoichiometric coefficient of $i$ , reaction $j$
$\mu_{i,j'}$	Stoichiometric coefficient of $i$ reaction $j'$
$\mu_{m,j}$	Stoichiometric coefficient of $m$ , reaction $j$
$\mu_{m,j'}$	Stoichiometric coefficient of $m$ , reaction $j'$
$\mu_{i,n(i,m)}$	Stoichiometry of $i$ in reaction $n$ with $m$
$\mu_{m,n(i,m)}$	Stoichiometry of $m$ in reaction $n$ with $i$
$v$	Mass conservation normalization factor for equilibration

## List of Symbols, Transport Equations

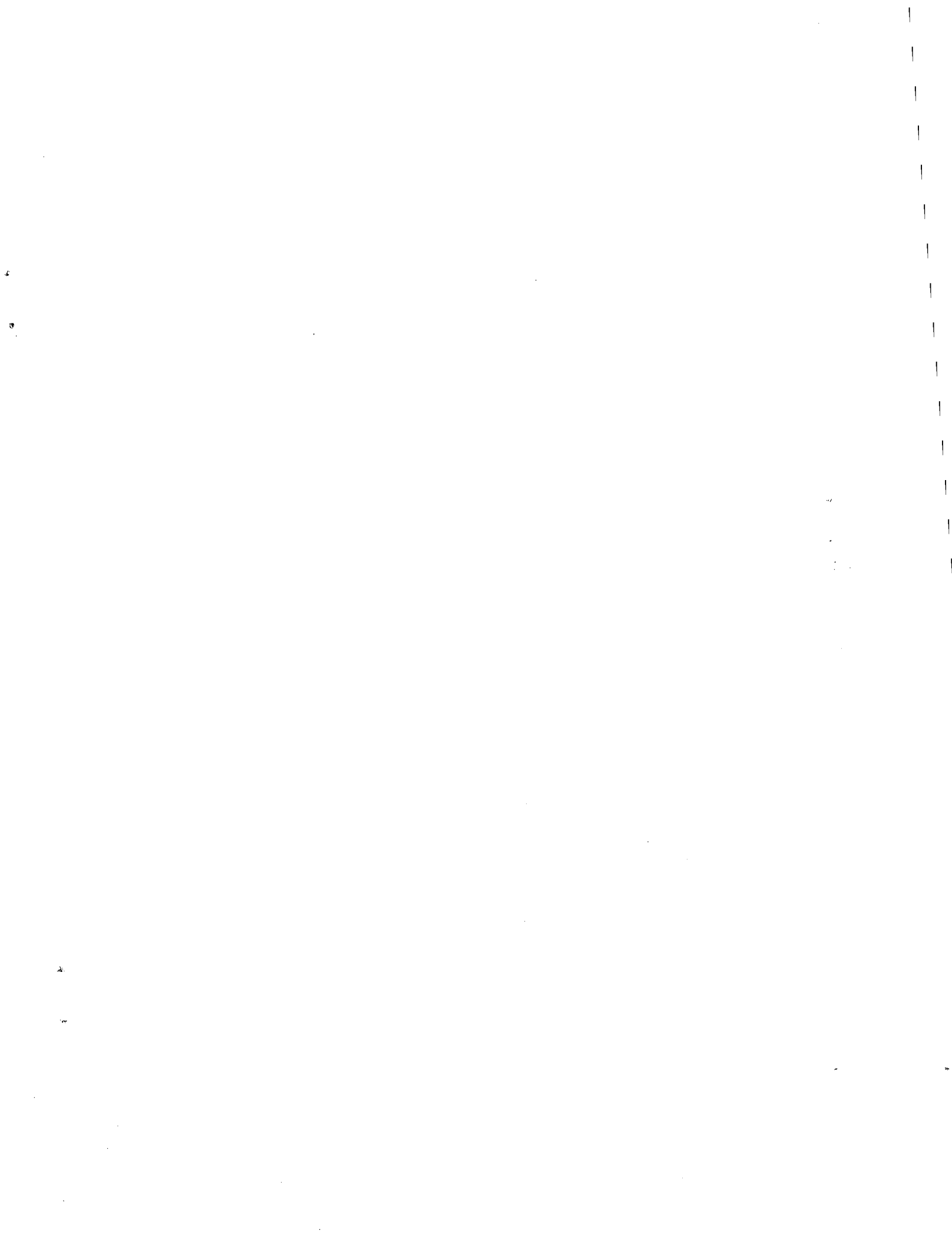
Symbol	Definition
$A_{l,m}$	Interfacial area between nodes $l$ and $m$
$\bar{c}_{l,m}^i$	Average concentration of $i$ at interface between $l$ and $m$
$D_d^i$	Effective diffusion coefficient for $i$
$D_H^i$	Hydrodynamic dispersion coefficient for $i$
$F_{l,m}$	Advectance between nodes $l$ and $m$
$G_l^i$	Source/sink term for species $i$
$K_d^i$	Distribution coefficient for species $i$
$n$	Material porosity
$q_{l,m}$	Darcy velocity between $l$ and $m$ , normal to interface
$R_i$	Retardation coefficient for species $i$
$U_{l,m}$	Conductance between nodes $l$ and $m$
$V_{B,l}$	Bulk volume of node $l$
$x_l$	Distance from nodal point $l$ to interface
$x_{l,m}$	Distance between nodal points $l$ and $m$
$x_m$	Distance from nodal point $m$ to interface
$\Delta c_{l,m}^i$	Spatial concentration gradient for $i$ between nodes $l$ and $m$
$\Delta c^i$	Temporal change in species $i$
$\Delta t$	Discrete time step
$\rho_b$	Material bulk dry density

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BERKELEY, CALIFORNIA 94720