DEVELOPMENT AND APPLICATION OF A MULTI-SUBSTRATE, MULTI-OPTION GROUNDWATER TRANSPORT MODEL FOR UNCERTAINTY ANALYSIS

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PREFACE

Using a computer model to simulate groudwater contaminant transport and fate has become a common practice in recent years. The modeling process may be divided into two areas; model development and model application. There are several important factors governing each area. For the development aspect, three components are essential; 1) the understanding of various mechanisms affecting the transport, and the derivation of mathematical equations to represent the actual processes. 2) efficient methods to solve resulting methemetical equations. 3) high speed computers to carry out the mathematical computations. Given the current availability of mathematical methods and recent rapid increase in computer speed, the first component appears to become a controlling factor. Thus, more precise description of fundamental transport mechanisms and the ability to incorporate these mechanisms into the transport process become a vital factor to model development. In addition, the cooperation among different scientific areas such as environmental engineering and science, microbiology, soil science, mathematics, and computer science is also important. For the application aspect, the success in using a model to simulate real world problems relies upon the selection of appropriate models and the use of accurate parameters. This requires the model user to understand what conditions a model is based upon, and whether these conditions reflect actual situations. For a given model selection, the ability of the model to simulate the reality depends upon the accuracy of input parameters.

This dissertation attempted to address the two modeling areas; model development and application. For the model development, the main effort was to incorporate various theories for adsorption and biological decay into the model. This includes different adsorption isotherms, non-equilibrium mass transfer, various biological decay functions, as well as secondary substrate utilization and oxygen transport. For the model application, the effort has focused upon the analysis of uncertainties resulting from model and parameter selections for the adsorption process. It must be stipulated that the primary objectives for this dissertation was for prove of concept. Potential users of the results of this research are cautioned that although the theories incorporated into the model have been used to address practical problems in various fields, that, as with all current codes, there are still discrepancies between these theories and actual processes. Applications of these theories to groundwater transport are contingent upon the assumption that the actual conditions in groundwater must comply with those under which the respective algorithms were derived.

This dissertation was divided into two chapters and an appendix. The first chapter described the development of the model while the second addressed the model uncertainties. Each chapter was written in approximate format for subsequent submittal to peer reviewed journals. This dissertation format can be conveniently modified for publication.

In the first chapter, a user friendly, finite difference groundwater transport model, named "Multi-substrate, Multi-option Groundwater Transport Model (MMGTM)", was developed in an attempt to achieve two goals: to include mechanisms not yet addressed by most current models and to provide a tool which could be used to simulate contaminant transport under a variety of conditions. In addition to advective-dispersive transport phenomena, the model can simulate adsorption and biological decay based on various mechanisms. Adsorption can be simulated for linear, Langmuir, or Freundlich isotherms coupled with equilibrium or non-equilibrium mass transfer. Biological decay can be simulated for first order or

Monod type approaches, and can be linked to oxygen consumption and transport. Decay of substrate in the aqueous as well as solid phases can be simulated. Two substrates and oxygen can be simulated simultaneously and the interaction between primary and secondary substrates can be described as competitive, diauxic-like or simultaneous. The growth of biomass and its effect as an adsorbent can also be simulated by means of a stochiometric yield coefficient and a biomass/adsorbent conversion factor. Continuous or pulse input of solute in conjunction with either constant mass flux or constant concentration boundaries can be selected to suit an actual problem. All or part of the above functions can be selected from menu screens, as deemed appropriate by the user. Parameters can be input line by line within the model or called from a separate data file. The input data can be viewed, modified and saved before actual simulation. Output is visually displayed on the screen as breakthrough and profile curves, while also being saved in an ASCII file for subsequent viewing or printing. The model is menu driven with on-screen instructions and can be run on IBM Personal Computers or compatibles.

In the second chapter, preliminary sensitivity and uncertainty analyses were performed to examine the effects of adsorption model and parameter selection on the groundwater transport process. The effects of parameter uncertainty and model selection were analyzed in conjunction with different boundary input conditions. As expected, it was found that the retardation factor generally postponed the arrival of contaminant in the continuous boundary input conditions but did not attenuate the final concentration. Pulse boundary input conditions, however, not only postponed the arrival of contaminant but also reduced the peak concentration. For non-equilibrium adsorption, a smaller overall mass transfer coefficient (r) tended to have a slower but longer adsorption effect, compared to a larger value. As a result, breakthrough curves with a smaller r's showed a higher liquid phase concentration in the earlier time periods, and lower concentrations in later periods, compared to the breakthrough curves developed from larger mass transfer coefficients, or from equilibrium assumptions. While the sensitivity for r may be relatively small compared to that for the retardation factor, the overall effect on output concentration was still considerable when the wide range of possible values was considered.

The analyses also showed that local sensitivity maximums existed for specific r values, which would make first order uncertainty analysis unsuitable for this situation. Comparisons between equilibrium and non-equilibrium models showed that in the period $0 < T \leq R$ equilibrium assumptions always under estimated the concentration predicted by non-equilibrium models. A maximum error of -100% was possible given parameter selection. For the period of $R < T \leq 2R$, the equilibrium assumption may either under or over estimate the output concentration, with a maximum possible negative error of -50% and positive error of 25%. After $T > 2R$, the equilibrium assumption always over estimated the concentration generated by non-equilibrium analysis, with a maximum error of 25%. Specifically, the mean error was less than 5% when the overall mass transfer coefficient was greater than 0.002 and 0.007/day for continuous and pulse boundary input, respectively, but a rapid increase in error was observed for both boundary conditions when the values of mass transfer coefficient decreased.

The results of model uncertainty analysis suggested that the indiscriminate use of linear equilibrium models may cause significant errors, especially when slow mass transfer dominates the adsorption process. An alternative non-equilibrium approach seemed necessary in this situation. This finding encourages future research work in the area of understanding adsorption kinetics in groundwater systems and in determining the mass transfer coefficients for a variety of marginally hydrophilic compounds.

I wish to express my sincerest and deepest appreciation to Dr. William F. McTernan, my major adviser, for his intelligent guidance, constant inspiration, and invaluable advice throughout my graduate study and research. Without these and and his research funding, my graduate study would not have been possible.

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CHAPTER I

MULTI-SUBSTRATE, MULTI-OPTION GROUND WATER TRANSPORT MODEL

MULTI-SUBSTRATE, MULTI-OPTION GROUND WATER TRANSPORT MODEL

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ABSTRACT

A user friendly, finite difference groundwater transport model, named "Multi-substrate, Multi-option Groundwater Transport Model (MMGTM)", was developed in an attempt to achieve two goals: to include mechanisms not yet addressed by most current models and to provide a tool which can be used to simulate contaminant transport under a variety of conditions. In addition to the advective-dispersive transport phenomena, the model can simulate adsorption and biological decay based on various mechanisms. Adsorption can be simulated for linear, Langmuir, or Freundlich isotherms coupled with equilibrium or non-equilibrium mass transfer. The biological decay can be simulated for first order or Monod type approaches, and be linked to oxygen consumption and transport. Substrate in the aqueous phase as well as that adsorbed on the solid phase can be simulated for biological decay. Two substrates and oxygen can be simulated simultaneously and the interaction between primary and secondary substrates can be described as competitive, diauxic-like or simultaneous. The growth of biomass and its effect as an adsorbent can also be simulated by means of a stochiometric yield coefficient and a biomass/adsorbent conversion factor. Continuous or pulse input of solute in conjunction with either constant mass flux or constant concentration boundaries can be selected to suit an actual problem. All or part of the above functions can be selected from menu screens, as deemed appropriate by the user. Parameters can be input line by line within the model or called from a separate data file. The input data can be viewed, modified and saved before actual simulation. Output is visually displayed on the screen as breakthrough and profile curves, while also being saved in an ASCII file in a disk for subsequent viewing or printing. The model is menu driven with on-screen instructions and can be run on IBM Personal Computers or compatibles.

INTRODUCTION

Modeling of the transport and fate of ground water contaminants is an important strategy in ground water pollution control. An accurate model can provide useful information for hazardous site cleanup, general ground water management, and regulatory use.

Numerous ground water transport models have been developed in recent years (Grove and Stollenwerk, 1987). Although most of the models originated from a specific pollution problem or for a specific contaminant, efforts have also been made to develop models for general contamination problems. Konikow and Bredehoeft (1978) developed a two dimensional model (MOC model) to simulate the effects of advection, dispersion and linear equilibrium adsorption of contaminants. Subsequently Prickett *et al* (1981) developed the Random Walk model to address dispersion in an alternative manner while also retaining linear adsorption. Srinivasan and Mercer (1987) developed the Bio1D model, which simulates the effects of dispersion, non-linear equilibrium adsorption and biological decay while Rifai *et al* (1989) developed the two dimensional BIOPLUME model to simulate the effects of linear-equilibrium adsorption and biological decay. While the development of these later models, and others, have improved the simulation of ground water transport by allowing more realistic approximations of biological processes, deficiencies in two general areas still exist. First, many models lack the ability to simulate certain mechanisms governing the transport, like the interaction of non-equilibrium adsorption and biological decay. Second, many of these models were developed under a specific set of conditions, and it is impossible to use a single model to simulate the transport of contaminants under various assumptions and conditions. A new model is presented which attempts to overcome these deficiencies.

Modeling of contaminant transport requires the appropriate description and treatment of various mechanisms affecting transport including advection, dispersion, adsorption and biological decay. While most models handled the advection and dispersion similarly, they differed in treatment of adsorption and biological decay. The MOC model assumed a linear and equilibrium adsorption and no biological decay. While the linear, equilibrium assumptions simplified the adsorption effect as a "retardation factor", the application has limited overall utility. Linear adsorption may be applicable to situations where the concentration of adsorbate is relatively low, but in other cases adsorption may not be linear. The commonly used adsorption isotherms, Langmuir or Freundlich, for example, are non-linear. Further, when evaluated in terms of contaminant loading rates, the linear isotherm does not allow for any decrease in the mass transported as adsorptive capacity is reached. The equilibrium assumption may be appropriate only for the situation where the mass transfer rate of solute from liquid to the solid is fast related to the groundwater flow. Freeze and Cherry (1979) described the effect of non-equilibrium adsorption on the transport of groundwater contaminants. It was found that the concentration front of the contaminants moves faster for non-equilibrium adsorption than for equilibrium adsorption. While the equilibrium assumption tends to overestimate the adsorption effect on contaminant transport, little effort has been made to quantitatively compare the effects of equilibrium or non-equilibrium adsorption on contaminant transport, partially due to a lack of appropriate models.

Biological decay of contaminants in an aquifer has been found, and its effects on contaminant transport have been vigorously investigated (Britton and Gerba, 1984; Borden *et al*, 1986; Borden and Bedient, 1987). It has been employed for *in situ* treatment options for aquifer restoration (Wilson *et al.* 1986). The inclusion of biodecay in transport models appears necessary to more closely approximate conditions found in some aquifer systems. Bio1D included biodecay with non-linear adsorption, but still assumed equilibrium adsorption. BIOPLUME, a modification of MOC, added the biological effects with linear equilibrium adsorption. To the authors' knowledge, there has not been a model developed that incorporates non-linear, non-equilibrium adsorption effects with biological decay of multiple substrates.

The fate of the sorbed substrate also needs to be addressed in simulation. Most transport models with biological decay functions only simulate the aqueous phase while ignoring the decay of the sorbed substrate. An implication is that the substrate becomes refractory once sorbed, which may not always hold. The substrate on solid phase, like that in solution, may also be subject to biological decay, in some cases at rates in excess of those in the solution due to increased concentration. This is a dynamic process, with substrate continuously transferred from the aqueous phase to the adsorptive medium with the sorbed and soluble substrates undergoing decay. This process may be further complicated by non-equilibrium mass transfer processes, which lead to the situation that the solid phase concentration is never saturated to the degree determined by the adsorption isotherm.

Another component neglected by other models is the effect of biomass on adsorption. The biomass may increase as the substrate degrades. According to accepted theory, the ultimate partition coefficient is a product of the soil organic coefficient (k_{OC}) and the soil organic content (f_{OC}). Increased biomass, which adds to the soil organic matter, can serve as an adsorbent. A stoichiometric calculation of biomass can be made from the yield coefficient, and the increased biomass can be regarded as an extra adsorptive medium and be converted into equivalent aquifer material.

Two purposes were addressed when developing this model: First, the model should be capable of simulating more complicated situations not provided for by currently available codes and second, the code should be capable of applying various combinations of transport functions to suit different transport conditions. Within the same model format, the user can conveniently select various simulation levels, from the simple advective-dispersive transport to the most complicated situations. It was intended to provide a tool for users who want to evaluate and compare, theoretically or practically, the effects of different conditions and hypotheses on contaminant transport.

User friendliness has often been neglected in many models. Regardless of internal sophistication, many do not interact with the user during operation. To overcome this weakness, the entire operation of this model is menu-driven with on-screen instructions. Since the model is self-explanatory, it can be used without frequent reference to a printed manual. The output is plotted on the screen also.

An improvement of input processes was also made. Many numerical models require a separate data file as input. The file may be prepared by a common text editor or a "preprocessor" provided with the model. Usually the data cannot be modified during execution of the program. In this model, the input file is made within the program. Once an input file is created, it can be modified for later use without going through the entire input process. Input data can be viewed and edited within the program and saved for later use.

MODEL DEVELOPMENT

Mass Balance Equations

The formulation of contaminant transport equations for the model was based on concepts of mass balance. The following equations were derived for non-equilibrium adsorption with solid and aqueous phase biological decay in conjunction with advective-dispersive transport. Other equations will be formed as the result of other simulation options selected by the user. While these other formulations were not included in the paper for the sake of brevity, they were used in the model according to the simulation option selected.

Figure 1 indicates the mass balance for a segment of one dimensional flow.

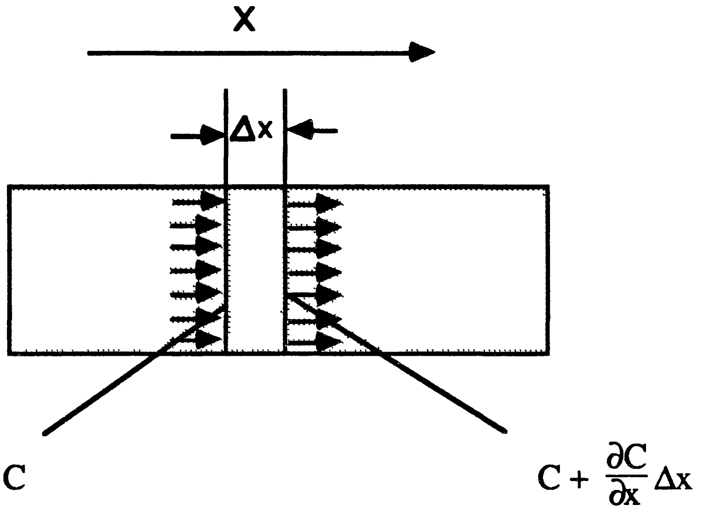


Figure 1. Mass Balance for Aqueous Phase Substrate Transport

The aqueous phase mass accumulation in segment Δx is expressed as (the meaning of simbols is listed in nomenclature):

$$A_c = J_{in} - J_{out} - (A + B) \tag{1}$$

Where:

$$A_c = \varepsilon\, S\, \Delta x\, \frac{\partial C}{\partial t} \tag{2}$$

$$J_{in} = \varepsilon\, S\, \Delta x\, C\, U - \varepsilon\, S\, D\, \frac{\partial C}{\partial x} \tag{3}$$

$$J_{out} = \varepsilon\, S\, U\, (C+\Delta x\, \frac{\partial C}{\partial x}) - \varepsilon\, S\, D \frac{\partial\, (C+\frac{\partial C}{\partial x}\, \Delta x)}{\partial x}$$

$$= \varepsilon\, S\, U\, (C+\Delta x\, \frac{\partial C}{\partial x}) - \varepsilon\, S\, D\, (\frac{\partial C}{\partial x} + \frac{\partial^2 C}{\partial x^2}\, \Delta x) \tag{4}$$

$$A = S\,(1-\varepsilon)\,\Delta x\;R\,(q^*-q)\,\frac{\rho_b}{1-\varepsilon} \tag{5}$$

$$B = \varepsilon\,S\,\Delta x\;F(C,O) \tag{6}$$

Substituting (2)-(6) into (1), and rearranging we get:

$$\frac{\partial C}{\partial t} = -U\,\frac{\partial C}{\partial x} + D\,\frac{\partial^2 C}{\partial x^2} - Fa(C,O) - \frac{\rho_b}{\varepsilon}\,R\,(q^*-q) \tag{7}$$

A similar mass balance expression is applied to the oxygen but ignores the adsorption of oxygen to the solid. The mass balance differential equation is then expressed as:

$$\frac{\partial O}{\partial t} = -U\,\frac{\partial O}{\partial x} + Do\,\frac{\partial^2 O}{\partial x^2} - f\,Fa(C,O) \tag{8}$$

In the solid phase, the accumulation of substrate is equal to the gain from adsorption from the aqueous phase minus the loss through the solid phase decay. The mass balance equation is expressed as:

$$\frac{\partial q}{\partial t} = R(q^*-q) - \frac{\varepsilon}{1-\varepsilon}\,\frac{1}{\rho_b}\,Fs(q,O) \tag{9}$$

In order to solve Equations (7), (8), and (9), the mathematical expressions for the adsorption and biological decay terms must be known. These terms are discussed in the following paragraphs.

Adsorption

Adsorption is the process in which the solute in the aqueous phase is transferred to the solid phase. It can be generally expressed by one of the three isotherms; linear, Langmuir, or Freundlich. The isotherms describe the equilibrium distribution of substrate between the aqueous and solid phases.

Linear Adsorption

The linear adsorption isotherm can be expressed as:

$$q = \frac{m_x}{m} = k_d C \tag{10}$$

The linear isotherm indicates that the solute concentration in the solid phase is proportional to the concentration in the aqueous phase. The adsorption of some organics onto soil at low concentration was reported to be linear (Means *et al* , 1980; Hassett *et al* , 1980). The distribution coefficient, k_d, can be obtained from experimental batch isotherm studies, or from correlation of soil organic contents, as proposed by Karichhoff *et al* (1979), Means *et al* (1980), and Schwarzenbach *et al* (1981). One of the correlation methods employed is to obtain the octanol/water partition coefficient for the solute, k_{ow}, modify it to k_{oc}, then multiply it with f_{oc} , as indicated below:

$$k_{ow} = C_o/C_w \tag{11}$$

$$k_{oc} = a \log (k_{ow}) + b \tag{11a}$$

$$k_d = k_{oc} f_{oc} \tag{11b}$$

Langmuir Adsorption

The Langmuir isotherm is derived from the assumption of a homogeneous monolayer of adsorbate on the adsorbent. It is widely used to describe adsorption onto activated carbon, both in chemical engineering applications and in water/wastewater treatment. It has been also employed to describe the adsorption of solute to soils and sediments. This isotherm can be expressed as:

$$q = \frac{m_x}{m} = \frac{Q\,k_L\,C}{1 + k_L\,C} \tag{12}$$

The constant Q and K_L can be determined by inverting equation (12):

$$\frac{1}{q} = \frac{1}{Q\,k_L\,C} + \frac{1}{Q} \tag{12a}$$

A straight line can be obtained by plotting $\frac{1}{q}$ versus $\frac{1}{C}$, where the slope is equal to $\frac{1}{Q\,k_L}$ and the intercept equals $\frac{1}{Q}$. The equilibrium aqueous concentration C and solid concentration q are measured in batch experimental adsorption studies.

Freundlich Adsorption

The Freundlich isotherm is a widely used empirical expression often applied to natural systems as well as activated carbon adsorption and has the form:

$$q = \frac{m_x}{m} = k\,C^{1/n} \tag{13}$$

When n = 1, the Freundlich isotherm is linear, k becomes k_d and equation (13) becomes identical to equation (10). The constants k and $\frac{1}{n}$ can be determined by taking the logarithms of both sides of equation (13):

$$\log (q) = \log (k) + \frac{1}{n} \log C \tag{13a}$$

A straight line can be obtained by plotting log(q) versus log (C), where the slope is equal to $\frac{1}{n}$ and the intercept equal to log (k). As with the Langmuir isotherm, q and C are measured in experimental batch isotherm studies.

The applicability of a particular isotherm depends upon the properties of the adsorbate and adsorbent. Batch isotherm studies can determine which isotherm is more appropriate. MMGTM uses any one of the linear, Langmuir, or Freundlich isotherms to simulate the adsorption process at the user's choice.

Adsorption Kinetics

While isotherms describe equilibrium relationships between the solute concentration in aqueous and solid phases, the process by which the solute is being transferred from the aqueous phase to the solid phase, or from solid phase to aqueous phase, must be addressed by kinetic models. The transfer generally includes three steps: 1) solute transfer from the bulk liquid to the liquid-solid interface, 2) solute diffusion along pores and solid surfaces, 3) solute adsorption onto the solid. These three processes proceed sequentially. Each of the steps is time dependent , and the slowest step controls the entire process. The process is said to be controlled by external resistance if step 1 is the slowest, and controlled by internal resistance if step 2 is the slowest. Step 3, however, rarely controls the process as it proceeds quickly. To further complicate matters, evidence exists that the chemical interaction between solute and solid in soils high in humic materials is partitioning rather than adsorption (Wershaw, 1986). If true, this transfer process could then be controlled by the internal resistance, which can be expressed as (Hines and Maddox, 1985):

$$\frac{\partial q}{\partial t} = k_S A_S (q^* - q) \tag{14}$$

When an overall mass transfer coefficient, R, is used to represent K_S and A_S:

$$R = k_S A_S \tag{14a}$$

Equation (14) then becomes:

$$\frac{\partial q}{\partial t} = R (q^* - q) \tag{14b}$$

The use of overall mass transfer coefficient R makes it possible to determine the coefficient by simple batch adsorption studies without knowing the specific surface area, A_S, which is difficult to measure. In simulating non-equilibrium adsorption process, MMGTM employs equation (14b), coupled with one of the isotherm expressions (equation (10), (12), or (13)), as chosen by the user.

Biological Decay

Biological decay of contaminants has been used for wastewater treatment for many decades. However, the application to ground water contamination did not begin until recent years. Aquifers have generally been regarded as devoid of oxygen and microbial activity In recent years, however, improved techniques for bacterial analysis indicated that some aquifers are biologically active (Wilson *et al*, 1983). Simultaneously, aerobic and anaerobic biodegradation investigations were compared, and some contaminants thought previously to be refractory were found to be biodegradable (Bouwer and McCarty, 1982; Vogel and McCarty, 1985). These efforts led to recognition of the possible importance of biodecay in ground water contaminant transport.

The major form of biodecay can be generally described as the process in which microorganisms use the contaminant as a carbon and energy source for their growth and maintenance. An electron acceptor must be reduced while the contaminant is oxidized. The electron acceptor may be oxygen, nitrate, sulfate, carbon dioxide, or even some organics. When oxygen is present and serves as the final electron acceptor, the process is called aerobic biodecay. Anaerobic biodecay occurs if species other than oxygen serve as electron acceptors. This model can simulate either aerobic or anaerobic processes or both (sequentially).

First Order Biodecay

First order reaction assumes that the disappearance rate of the substrate of interest is proportional to the concentration remaining. It is expressed as:

$$\frac{dC}{dt} = k_1 C \qquad (15)$$

The first order reaction simplifies the biological process and is adopted in some transport models due to its simplicity. However, first order biodecay is appropriate only when the substrate is the growth limiting factor and the bacterial concentration is relatively high.

Monod Biogrowth Model

Monod (1949) first proposed an empirical equation to describe bacterial growth rate:

$$u = \frac{u_{max}\, C}{k_h + C} \tag{16}$$

Biological growth can then be expressed as:

$$\frac{dM}{dt} = M \frac{u_{max}\, C}{k_h + C} \tag{17}$$

The utilization rate of substrate can be derived from equation (17) by linking it with the yield coefficient, which is the mass of bacteria generated per mass of substrate utilized. The utilization of substrate is then expressed as:

$$\frac{dC}{dt} = \frac{M}{Y_g} \frac{u_{max}\, C}{k_h + C} \tag{18}$$

Equation (18) assumes oxygen is not a rate limiting factor. When oxygen becomes rate limiting, modification is made by introducing an oxygen term. Rich (1973) modified the Monod equation by multiplying by a term, $\frac{O}{k_o + O}$, which assumed that the limiting effect of oxygen on the bacterial growth is similar to that of substrate.

It is also known that when substrate is below a minimum concentration, it cannot support the growth of the bacteria and utilization of the substrate may cease. Likewise, when the oxygen is below this minimum concentration, aerobic decay may cease and shift to anaerobic biodecay. The above concepts were incorporated in the modified Monod function to simulate aerobic biological decay:

$$F_a (C,O) = \frac{u_{max} M}{Y_g} \frac{C - C_{min}}{k_h + C} \frac{O - O_{min}}{k_o + O} \quad (C > C_{min} \text{ and } O > O_{min}) \tag{19}$$

$$F_a (C,O) = 0 \quad (C \leq C_{min} \text{ or } O \leq O_{min}) \tag{19a}$$

Anaerobic Biodecay

Anaerobic biodecay may occur when oxygen is absent or below the minimum concentration for aerobic biodecay. Anaerobic processes are usually considered slower than the corresponding aerobic decay. The equations describing anaerobic biodecay are similar to those for aerobic conditions where first order anaerobic biodecay is identical to equation (15) but with a smaller rate constant. Alternatively, anaerobic biodecay may also be described as:

$$\frac{dC}{dt} = \frac{k_{nmax} C}{k_{nh} + C} \tag{20}$$

The model can use either equation (15) or (20) to simulate anaerobic biodecay, at the user's selection.

Biodecay in Solid Phase

Biodecay in the solid phase is simulated by similar methods as biodecay in the aqueous phase. Biodecay in the solid phase is assumed to proceed simultaneously and independently to the aqueous phase biodecay, with the exception that for aerobic Monod option, the biodecay in both phases is linked to the oxygen, which is the final electron acceptor for both phases. Although the biodecay rates in both phases are a function of substrate concentration in each phase, they affect each other indirectly by the adsorption process, which determines the distribution of substrate between the two phases. For biodecay in the solid phase, the aqueous concentration

C is replaced by the solid phase concentration q, and equations (15), (19), (19a), and (20) become:

$$\frac{dq}{dt} = k_{s1}\, q \qquad (21)$$

$$F_s\,(q,O) = \frac{u_{smax}\, M}{Y_g}\;\frac{q - q_{min}}{k_q + q}\;\frac{O - O_{min}}{k_o + O} \qquad (22a)$$

$$(q > q_{min} \text{ and } O > O_{min})$$

$$F_s\,(q,O) = 0 \quad (\, q \le q_{min} \text{ or } O \le O_{min}) \qquad (22b)$$

$$\frac{dq}{dt} = \frac{kns_{max}\, q}{kns_h + q} \qquad (23)$$

Secondary Utilization

MMGTM can simulate secondary utilization by either first order or Monod expressions. For the first order biodecay option, the model simulates secondary utilization by linking its decay coefficient to the concentration of the primary substrate. There may be three different types of interaction between the primary and secondary substrates. In type 1, the decay of secondary substrate depends upon the utilization of the primary substrate. This is often the case when the concentration of secondary substrate is too low to support bacterial growth. When the primary substrate concentration is above a certain concentration, the bacteria utilize the primary substrate as primary carbon and energy source and simultaneously degrade the secondary substrate at a certain rate. When the concentration of the primary substrate drops below a certain minimal value, the growth of bacteria and utilization of the primary substrate may be hindered, and the utilization rate of secondary substrate may also decrease. In type 2, primary and secondary substrates are biodecayed simultaneously and independently with their own coefficients. There are no interactions between them. In type 3 , the biodecay of primary and secondary substrates is competitive. In this situation, the bacteria first attack the primary substrate, which is easier to degrade than the secondary. When the primary substrate is above a certain concentration, the decay of the secondary substrate is limited or nonexistent. If the primary substrate concentration decreases below a critical concentration, the biodegradation of secondary substrate increases. This type approximates diauxic growth described in classical bacteriology. The above interactions between primary and secondary substrates can be expressed as:

$$\frac{dC}{dt} = k21C \qquad (Cp > Cpo) \tag{24a}$$

$$\frac{dC}{dt} = k22C \qquad (Cp \leq Cpo) \tag{24b}$$

The coefficients k_{21} and k_{22} are defined as stage 1 and stage 2 first order biodecay coefficients for secondary substrate biodecay, respectively, and C_{po} is defined as primary break point concentration. The values of k_{21} and k_{22} depend upon the interaction type. When type 1 is simulated, $k_{21} > k_{22}$. Likewise, $k_{21} = k_{22}$ for type 2, and $k_{21} < k_{22}$ for type 3. When secondary substrate is simulated, the model checks the concentration of primary substrate at each time step, and uses the appropriate coefficient for secondary biodecay.

Numerical Solution

Equations (7), (8), and (9) were solved numerically by the method of finite difference approximation. The space differential terms were approximated by central difference scheme, also known as Crank-Nicholson Method. Mathematically this method provides a smaller truncation error and better stability than the forward or backward difference schemes. The resulting algebraic equations, however, are more complicated than those from the other two methods. Crank-Nicholson method was chosen because stability is the primary concern for the model development.

Finite Difference Approximation

The differential terms in equation (7) through (9) can be approximated as follows (the subscript i and j represents space and time nodes respectively):

$$\frac{\partial C}{\partial t} = \frac{(C_{i,j+1} - C_{i,j})}{\Delta t} \tag{24}$$

$$\frac{\partial C}{\partial x} = \frac{1}{2}\left[\frac{(C_{i+1,j} - C_{i-1,j})}{2\ \Delta x} + \frac{(C_{i+1,j+1} - C_{i-1,j+1})}{2\ \Delta x}\right] \tag{25}$$

$$\frac{\partial^2 C}{\partial x^2} = \frac{1}{2}\left[\frac{(C_{i-1,j} - 2\ C_{i,j} + C_{i+1,j})}{\Delta x^2} + \frac{(C_{i-1,j+1} - 2\ C_{i,j+1} + C_{i+1,j+1})}{\Delta x^2}\right] \tag{26}$$

$$\frac{\partial q}{\partial t} = \frac{(q_{i,j+1} - q_{i,j})}{\Delta t} \tag{27}$$

$$\frac{\partial O}{\partial x} = \frac{1}{2}\left[\frac{(O_{i+1,j} - O_{i-1,j})}{2\ \Delta x} + \frac{(O_{i+1,j+1} - O_{i-1,j+1})}{2\ \Delta x}\right] \tag{28}$$

$$\frac{\partial^2 O}{\partial x^2} = \frac{1}{2}\left[\frac{(O_{i-1,j} - 2\ O_{i,j} + O_{i+1,j})}{\Delta x^2} + \frac{(O_{i-1,j+1} - 2\ O_{i,j+1} + O_{i+1,j+1})}{\Delta x^2}\right] \tag{29}$$

For non-differential terms, the mean of the value at time j and time, j+1 is used:

$$Fa(C,O) = \frac{1}{2}\left[Fa\,(C_{i,j}\,,O_{i,j}) + Fa(\,C_{i,j+1}\;,\;O_{i,j+1})\,\right] \tag{30}$$

$$Fs(q,O) = \frac{1}{2}\left[Fs\,(q_{i,j}\,,O_{i,j}) + Fs\,(q_{i,j+1}\;,\;O_{i,j+1})\,\right] \tag{31}$$

Substituting (24) through (31) into (7) through (9):

$$\begin{aligned} f_i = &- \alpha C_{i-1,j+1} + \beta\, C_{i,j+1} + \gamma\, C_{i+1,j+1} - \alpha C_{i-1,j} + C_{i,j} + \gamma\, C_{i+1,j} - \\ &- \tau q_{i,j+1} + \tau q^*_{i,j+1} + \tau\, q^*_{i,j} - \tau q_{i,j} + \frac{1}{2} Fa(C_{i,j},O_{i,j}) + \\ &+ \frac{1}{2} Fa(C_{i,j+1},O_{i,j+1}) = 0 \end{aligned} \tag{32}$$

$$\begin{aligned} g_i = &-\alpha_1 O_{i-1,j+1} + \beta_1 O_{i,j+1} + \gamma_1 O_{i+1,j+1} - \alpha_1 O_{i-1,j} + \theta_1 O_{i,j} + \\ &+ \gamma_1 O_{i+1,j} + \frac{1}{2} f\; Fa(C_{i,j},O_{i,j}) + \frac{1}{2} f\; Fa(C_{i,j+1},O_{i,j+1}) + \\ &+ \frac{1}{2} f\; Fs(q_{i,j},O_{i,j}) + \frac{1}{2} f\; Fs(q_{i,j+1},O_{i,j+1}) = 0 \end{aligned} \tag{33}$$

$$\begin{aligned} h_i = &\;\mu\, q^*_{i,j+1} + \mu\, q^*_{i,j} - (1 + \mu) q_{i,j+1} + (1 + \mu) q_{i,j} - \\ &- \omega \frac{1}{2}\, Fs(q_{i,j},O_{i,j}) - \omega \frac{1}{2}\, Fa(q_{i,j+1},O_{i,j+1}) = 0 \end{aligned} \tag{34}$$

Where:

$$\alpha = \frac{D}{2\Delta x^2} + \frac{U}{4\Delta x^2} \qquad\qquad \gamma = \frac{U}{4\Delta x} + \frac{D}{2\Delta x^2}$$

$$\beta = \frac{D}{\Delta x^2} + \frac{1}{\Delta t} \qquad\qquad \theta = \frac{D}{\Delta x^2} - \frac{1}{\Delta t}$$

$$\omega = \frac{\varepsilon}{1-\varepsilon} \qquad \mu = \frac{R\Delta t}{2}$$

$$\alpha_1 = \frac{Do}{2\Delta x^2} + \frac{U}{4\Delta x^2} \qquad \beta_1 = \frac{Do}{\Delta x^2} + \frac{1}{\Delta t}$$

$$\gamma_1 = \frac{U}{4\Delta x} + \frac{Do}{2\Delta x^2} \qquad \theta_1 = \frac{Do}{\Delta x^2} - \frac{1}{\Delta t}$$

$$\tau = \frac{\rho_b R}{2\varepsilon}$$

The functions Fa, Fs, and q* represent the aqueous phase biodecay, solid phase biodecay, and adsorption, respectively. The specific values for these functions depend upon the options the user selects. The equations for these functions have been discussed previously.

Newton-Raphson Solution

Each of the equations 18 to 20 contains n algebraic equations (i = 1,2,....n), where n is the number of the space nodes. Therefore there are a total of 3 x n equations. The unknowns are $C_{i,j+1}$, $O_{i,j+1}$ and $q_{i,j+1}$, while $C_{i,j}$, $O_{i,j}$ and $q_{i,j}$ are known from initial conditions or previous calculations. These equations become non-linear when Langmuir or Freundlich adsorption and/or Monod biodecay is chosen by the user. Newton-Raphson Method was employed to solve these non-linear equations. The method transforms the non-linear equations into a set of linearized expressions, where each coefficient of the unknown is a partial derivative of one non-linear function about the corresponding unknown. The matrix form of the linearalized algebraic equation is known as a Jacobian Matrix:

$$
\left|\begin{array}{ccccccccc}
\frac{\partial f_1}{C_1} & \frac{\partial f_1}{\partial O_1} & \frac{\partial f_1}{\partial q_1} & \frac{\partial f_1}{\partial C_2} & & & & & \\
\frac{\partial g_1}{\partial C_1} & \frac{\partial g_1}{\partial O_1} & \frac{\partial g_1}{\partial q_1} & 0 & \frac{\partial g_1}{\partial O_2} & & & & \\
\frac{\partial h_1}{\partial C_1} & \frac{\partial h_1}{\partial O_1} & \frac{\partial h_1}{\partial q_1} & 0 & 0 & 0 & & & \\
\frac{\partial f_2}{\partial C_1} & 0 & 0 & \frac{\partial f_2}{\partial C_2} & \frac{\partial f_2}{\partial O_2} & \frac{\partial f_2}{\partial q_2} & \frac{\partial f_2}{\partial C_3} & & \\
 & \frac{\partial g_2}{\partial O_1} & 0 & \frac{\partial g_2}{\partial C_2} & \frac{\partial g_2}{\partial O_2} & \frac{\partial g_2}{\partial q_2} & 0 & \frac{\partial g_2}{\partial O_3} & \\
 & & 0 & \frac{\partial h_2}{\partial C_2} & \frac{\partial h_2}{\partial O_2} & \frac{\partial h_2}{\partial q_2} & 0 & 0 & 0 \\
 & & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\frac{\partial f_{n-1}}{\partial C_{n-2}} & 0 & 0 & \frac{\partial f_{n-1}}{\partial C_{n-1}} & \frac{\partial f_{n-1}}{\partial O_{n-1}} & \frac{\partial f_{n-1}}{\partial q_{n-1}} & \frac{\partial f_{n-1}}{\partial C_n} & & \\
 & \frac{\partial g_{n-1}}{\partial O_{n-2}} & 0 & \frac{\partial g_{n-1}}{\partial C_{n-1}} & \frac{\partial g_{n-1}}{\partial O_{n-1}} & \frac{\partial g_{n-1}}{\partial q_{n-1}} & 0 & \frac{\partial g_{n-1}}{\partial O_n} & \\
 & & 0 & \frac{\partial h_{n-1}}{\partial C_{n-1}} & \frac{\partial h_{n-1}}{\partial O_{n-1}} & \frac{\partial h_{n-1}}{\partial q_{n-1}} & 0 & 0 & 0 \\
 & & & \frac{\partial f_n}{\partial C_{n-1}} & 0 & 0 & \frac{\partial f_n}{\partial C_n} & \frac{\partial f_n}{\partial O_n} & \frac{\partial f_n}{\partial q_n} \\
 & & & & \frac{\partial g_n}{\partial O_{n-1}} & 0 & \frac{\partial g_n}{\partial C_n} & \frac{\partial g_n}{\partial O_n} & \frac{\partial g_n}{\partial q_n} \\
 & & & & & 0 & \frac{\partial h_n}{\partial C_n} & \frac{\partial h_n}{\partial O_n} & \frac{\partial h_n}{\partial q_n}
\end{array}\right|
\times
\left|\begin{array}{c}
\Delta C_1 \\ \Delta O_1 \\ \Delta q_1 \\ \Delta C_2 \\ \Delta O_2 \\ \Delta q_2 \\ \cdot \\ \cdot \\ \cdot \\ \Delta C_{n-1} \\ \Delta O_{n-1} \\ \Delta q_{n-1} \\ \Delta C_n \\ \Delta O_n \\ \Delta q_n
\end{array}\right|
=
\left|\begin{array}{c}
f_1 \\ g_1 \\ h_1 \\ f_2 \\ g_2 \\ h_2 \\ \cdot \\ \cdot \\ \cdot \\ f_{n-1} \\ g_{n-1} \\ h_{n-1} \\ f_n \\ g_n \\ h_n
\end{array}\right|
\qquad (35)
$$

where:

$$\frac{\partial f_i}{\partial C_{i-1}} = -\alpha \qquad \frac{\partial f_i}{\partial C_i} = \beta + \tau \frac{\partial q_i}{\partial C_i} + \frac{1}{2}\frac{\partial Fa_i}{\partial C_i}$$

$$\frac{\partial f_i}{\partial C_{i+1}} = \gamma \qquad \frac{\partial f_i}{\partial O_i} = \frac{1}{2}\frac{\partial Fa_i}{\partial O_i} \qquad \frac{\partial f_i}{\partial q_i} = \tau$$

$$\frac{\partial g_i}{\partial O_{i-1}} = -\alpha_1 \qquad \frac{\partial g_i}{\partial O_i} = \beta_1 + \frac{1}{2} f \frac{\partial Fa_i}{\partial O_i} + \frac{1}{2} f \frac{\partial Fs_i}{\partial O_i}$$

$$\frac{\partial g_i}{\partial O_{i+1}} = \gamma_1 \qquad \frac{\partial g_i}{\partial C_i} = \frac{1}{2} f \frac{\partial Fa_i}{\partial C_i} \qquad \frac{\partial g_i}{\partial q_i} = \frac{1}{2} f \frac{\partial Fs_i}{\partial q_i}$$

$$\frac{\partial h_i}{\partial q_i} = -(1+r) - \frac{\omega}{2} \frac{\partial Fs_i}{\partial q_i} \qquad \frac{\partial h_i}{\partial C_i} = r \frac{\partial q_i}{\partial C_i} \qquad \frac{\partial h_i}{\partial O_i} = -\frac{\omega}{2} \frac{\partial Fs_i}{\partial O_i}$$

The values of $\frac{\partial q_i}{\partial C_i}$, $\frac{\partial Fa_i}{\partial C_i}$, $\frac{\partial Fa_i}{\partial O_i}$, $\frac{\partial Fs_i}{\partial q_i}$, and $\frac{\partial Fs_i}{\partial O_i}$ depend upon the adsorption and biodecay options the user selected.

linear adsorption:

$$\frac{\partial q_i}{\partial C_i} = k_d$$

Langmuir adsorption:

$$\frac{\partial q_i}{\partial C_i} = \frac{Q\, k_l}{(1 + k_L\, C_i)^2}$$

Freundlich adsorption:

$$\frac{\partial q_i}{\partial C_i} = \frac{1}{n}\, k\, C_i^{(1/n)-1}$$

first order biodecay:

$$\frac{\partial Fa_i}{\partial C_i} = k_1 \qquad \frac{\partial Fs_i}{\partial q_i} = ks_1$$

$$\frac{\partial Fa_i}{\partial O_i} = 0 \qquad \frac{\partial Fs_i}{\partial O_i} = 0$$

aerobic Monod biodecay:

$$\frac{\partial Fa_i}{\partial C_i} = \frac{u_{max}\, M}{Y_g} \, \frac{O_i - O_{min}}{k_o + O_i} \, \frac{k_h + C_{min}}{(k_h + C_i)^2}$$

$$\frac{\partial Fa_i}{\partial O_i} = \frac{umax\ M}{Yg}\ \frac{C_i - Cmin}{kh + C_i}\ \frac{ko + Omin}{(ko + O_i)^2}$$

$$\frac{\partial Fs_i}{\partial q_i} = \frac{usmax\ M}{Yg}\ \frac{O_i - Omin}{ko + O_i}\ \frac{kq + qmin}{(kq + q_i)^2}$$

$$\frac{\partial Fs_i}{\partial O_i} = \frac{usmax\ M}{Yg}\ \frac{q_i - qmin}{kq + q_i}\ \frac{ko + Omin}{(ko + O)^2}$$

anaerobic Monod biodecay:

$$\frac{dC}{dt} = \frac{knmax\ C}{knh + C}$$

In each time step, an initial value of C, O, and q is selected. Based on these values, the numerical value of each element of the Jacobian matrix and the right hand side column matrix is calculated. Given these values, the equation set (35) is solved for ΔC, ΔO, and Δq, by the Gauss elimination method. The values of initial trials are modified as follows:

$$C_i = C_i - \Delta C_i \qquad (36a)$$

$$O_i = O_i - \Delta O_i \qquad (36b)$$

$$q_i = q_i - \Delta q_i \qquad (36c)$$

The modified values, being closer to the true solution, are then used to substitute for the initial trial. The process is repeated until the maximum value of ΔC, ΔO, and Δq is less than a specified error tolerance. The simulation then moves to the next time step, and again repeats the trial-modification process.

Approximation of Biological Growth

To simplify the mathematical procedure, two assumptions were made in simulation of biological growth. First, the biomass is attached to each compartment specified by the user as space node. That is, it is not transported by advection or dispersion, as do the solutes. Secondly, the biomass is assumed constant during each simulation step. Only after the simulation of each time step is completed, the amount of biomass is evaluated based on the gain or loss due to substrate utilization and self-decay during the time period Δt.

The updated biomass was calculated from the following equation:

$$M_{i,j+1} = M_{i,j} + Gr_i - De_i \tag{37}$$

Where Gr and De are the amount of biomass generated from growth and the amount lost by death, respectively, during period Δt. The term $Gr_i - De_i$ then is the net gain of biomass during the period. The gain of biomass due to substrate utilization is equal to the substrate utilization rate multiplied by the stoichiometric yield coefficient, and the loss of biomass due to death is equal to the amount of biomass present multiplied by the death rate coefficient. As with other functions in the model, the mean of the values at previous time j and at current time j+1 is used. The growth and death of biomass is then expressed as:

$$\begin{aligned} Gr_i = {} & \frac{(u_{max} M_{i,j} \Delta t)}{2} \frac{(C_{i,j} - C_{min})}{(k_h + C_{i,j})} \frac{(O_{i,j}) - O_{min}}{(k_o + O_{i,j})} + \\ & + \frac{(u_{max} M_{i,j+1} \Delta t)}{2} \frac{(C_{i,j+1} - C_{min})}{(k_h + C_{i,j+1})} \frac{(O_{i,j+1}) - O_{min}}{(k_o + O_{i,j+1})} + \\ & + \frac{(u_{max} M_{i,j} \Delta t)}{2} \frac{(q_{i,j} - q_{min})}{(k_h + q_{i,j})} \frac{(O_{i,j}) - O_{min}}{(k_o + O_{i,j})} + \\ & + \frac{(u_{max} M_{i,j+1} \Delta t)}{2} \frac{(q_{i,j+1} - q_{min})}{(k_h + q_{i,j+1})} \frac{(O_{i,j+1}) - O_{min}}{(k_o + O_{i,j+1})} \end{aligned} \tag{37a}$$

$$De_i = \frac{d_e \Delta t}{2} (M_{i,j} + M_{i,j+1}) \tag{37b}$$

The first two terms in equation (37a) represent the mean of biomass generated from aqueous phase utilization of substrate, and the last two from solid phase substrate utilization. The updated biomass, $M_{i,j+1}$, was calculated from the known biomass $M_{i,j}$, by solving equations (37, 37a, and 37b) simultaneously.

Effects of Biomass on Adsorption

The biomass generated from bacterial growth can also adsorb substrate like the existing adsorbent (aquifer material), while the parameters for adsorption isotherms or kinetics might be different. To simplify the simulation, the concept of "equivalent adsorbent" was used. The equivalent adsorbent is defined to be the mass of aquifer material which has the same maximum adsorption capacity as that of the biomass. A factor (f_a) was used to multiply the amount of biomass to convert it to equivalent adsorbent, where f_a is equal to the ratio of maximum adsorption capacity of biomass to that of the aquifer material. Then the equivalent adsorbent and the real adsorbent are added for adsorption simulation.

Boundary Conditions

Two types of boundary conditions can be applied to the model: constant mass flux and constant concentration. The constant mass may be expressed as:

$$D\frac{\partial C}{\partial x} + U\,C = U\,C_o \tag{38}$$

The finite difference form for the left boundary is:

$$-D\frac{C_2 - C_L}{2\Delta x} + U\,C_1 = U \tag{38a}$$

while the finite difference form for the right boundary is:

$$-D\frac{C_R - C_{n-1}}{2\Delta x} + U\,C_n = U\,C_n \tag{38b}$$

C_L and C_R are the concentration at nodes beyond the left and right boundaries (also known as fictitious nodes). They can be calculated from equations (38a) and (38b). These two values are applied to the space node 1 and node n respectively. Boundary conditions for oxygen are identical to equations (38a) and (38b), with oxygen concentration substituting for the substrate concentration.

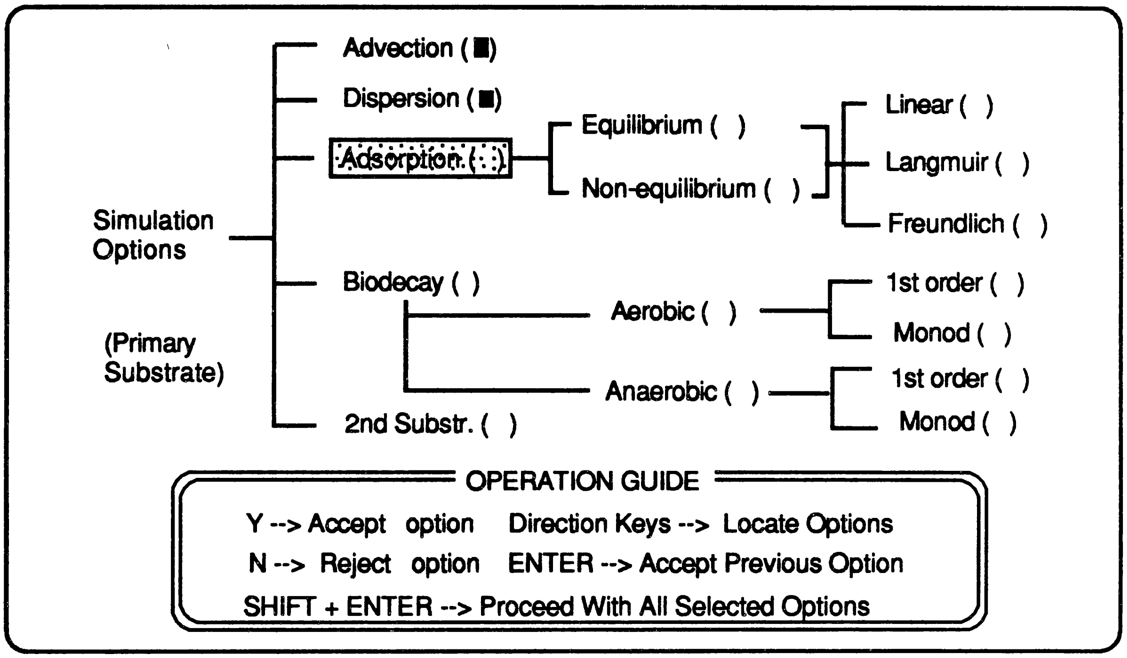
For constant concentration type left boundary:

$$C_L = C_0 \tag{39}$$

The right boundary is fixed for constant mass flux type (equation 38b), which is most appropriate for most actual applications.

Model Structure

As the model can simulate various combinations of adsorption and biodecay functions, an option menu (Figure 2) is displayed at the beginning of the program. The user can move the highlighted cursor across the screen to choose the desired simulation options. The subsequent screen prompts for required input only related to the selected options, thus eliminating unnecessary data input. The data can be viewed and modified within the program before simulation, with the selected options and input parameters being saved in two separate files. The output of the program is plotted on the screen as concentration (substrate and oxygen) versus time (breakthrough curves) and concentration versus space (profile curves) during execution with information being printed on the screen. This includes: the error for Newton-Raphson iterations, the current time step being executed, the number of nodes where stage 1 or stage 2 secondary substrate biodecay took place, and the number of nodes in which aerobic or anaerobic biodecay occurred. After simulation, the results are saved in an output ASCII file, which can be viewed on the screen or routed to the printer. The flowchart of program structure is shown in Figure 3 and an example output screen is shown in Figure 4.



Y --> Accept option   Direction Keys --> Locate Options
N --> Reject option   ENTER --> Accept Previous Option
SHIFT + ENTER --> Proceed With All Selected Options

Figure 2. The Simulation Option Screen for the Model

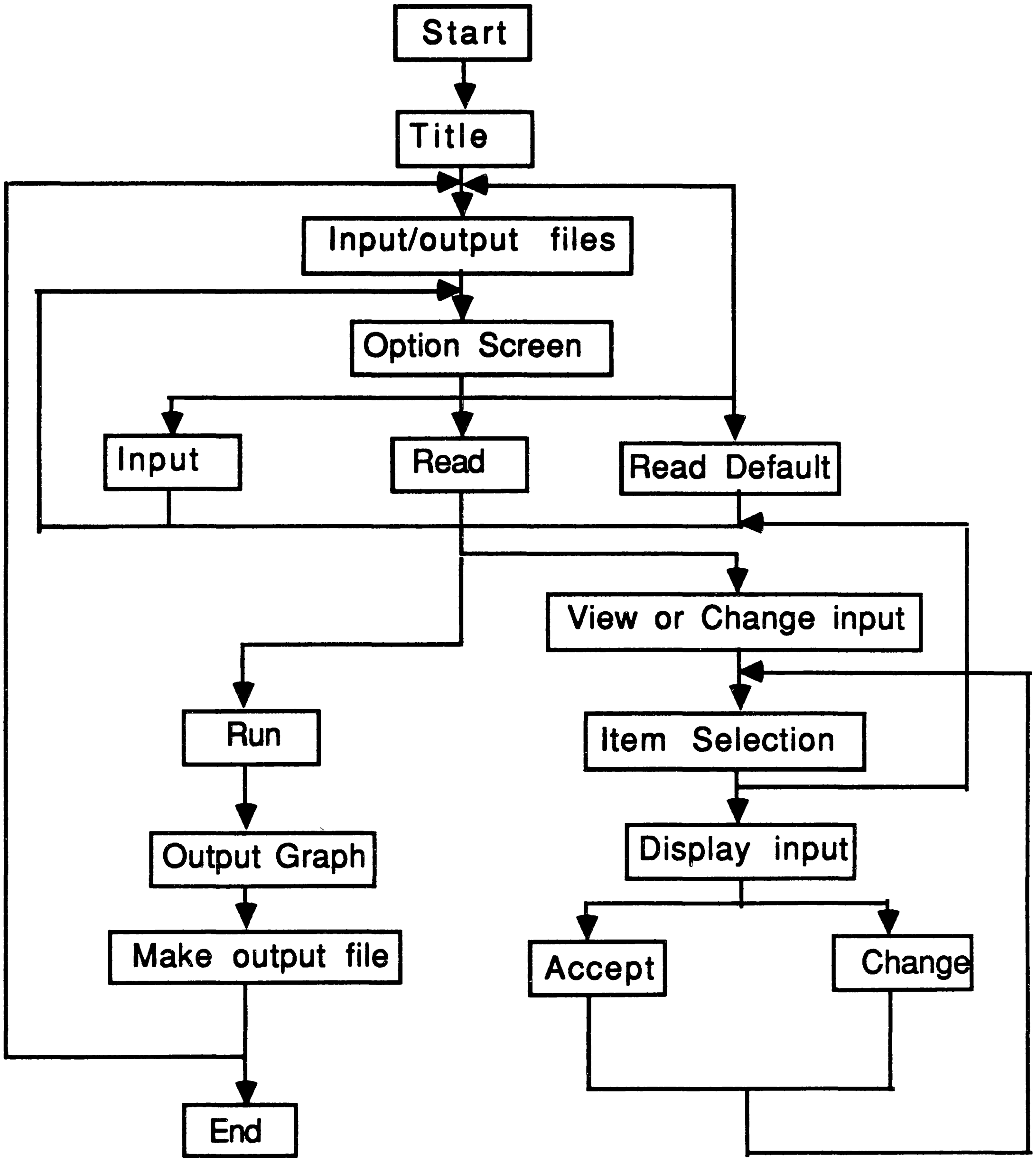


Figure 3. Flowchart of the Model Structure

EXAMPLE SIMULATION

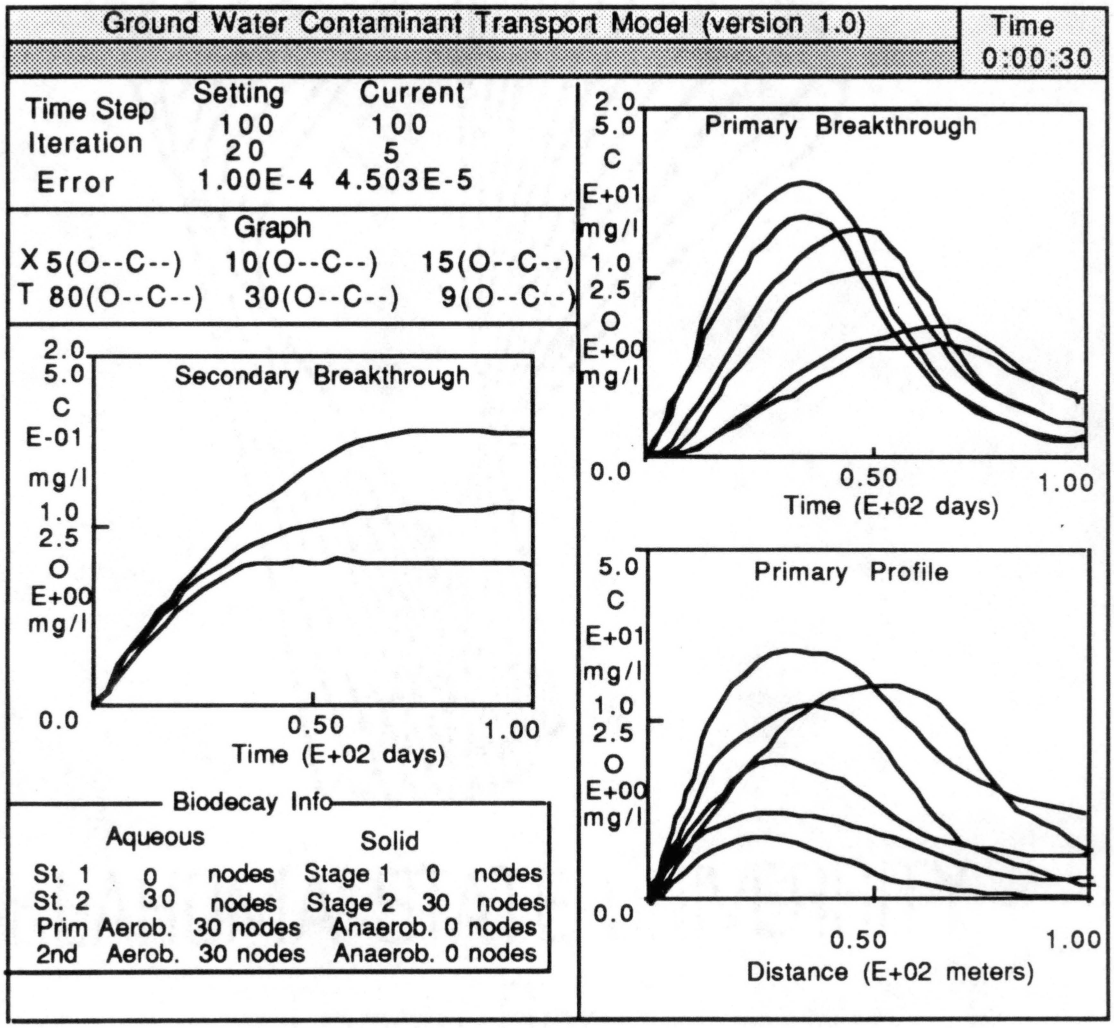
For illustrative purposes a set of example data files was employed in simulation. These files demonstrate the full simulation capacity, which includes non-equilibrium adsorption, aqueous and solid phase biodecay, oxygen consumption and transport, and secondary substrate utilization. The options and input parameters of the sample files are shown in Tables I and II with the corresponding output shown in Figures 5 to 8.

Figure 5 shows the breakthrough curves of primary substrate and oxygen at three spatial nodes. The breakthrough curves of secondary substrate are shown in Figure 6, for the same spatial nodes as for primary substrate. A maximum of three spatial nodes, reflecting the distance from the boundary for the corresponding breakthrough curves, can be selected by the user as input data.

The profile curves for primary substrate and oxygen at three temporal nodes are shown in Figure 7, while the profile curves for secondary substrate at the same temporal nodes are shown in Figure 8. Analogous to the spatial nodes for breakthrough curves, the temporal nodes reflect the time for the corresponding curves. A maximum of three temporal nodes can be chosen as input data.

While all data for Figures 5 to 8 are saved in an output file, Figures 5 to 7 are also plotted on the screen during excution of the program. Figure 8, however, is not displayed on the screen during excution due to space limitation.

There are some softwares in the market which can capture the output screen and route it to the printer. The breakthrough and profile curves from the screen or printer are useful for conveneient comparison among different simulations. For more precise work, the user can retrieve and handle the output data with spread sheet softwares such as Microsoft Excel or Lotus 1-2-3.



Ground Water Contaminant Transport Model (version 1.0)

Time
0:00:30

	Setting	Current
Time Step	100	100
Iteration	20	5
Error	1.00E-4	4.503E-5

Graph
X 5(O--C--) 10(O--C--) 15(O--C--)
T 80(O--C--) 30(O--C--) 9(O--C--)

Biodecay Info

Aqueous			Solid		
St. 1	0	nodes	Stage 1	0	nodes
St. 2	30	nodes	Stage 2	30	nodes
Prim Aerob.	30	nodes	Anaerob.	0	nodes
2nd Aerob.	30	nodes	Anaerob.	0	nodes

Figure 4. Output Screen of the Model

Table I. Input Parameters Primary Substrate and Oxygen

OPTIONS

Advection (yes)
Dispersion (yes)
Adsorption (yes, linear, non-equilibrium)
Biodecay (yes, Aerobic, Monod)
Secondary Substrate (yes)

PARAMETERS

Linear adsorption coeff.	0.1	cm^3/gm
Mass transfer coeff. for adsorption	1.0	day^{-1}
Min. oxygen conc. for aerobic biodecay	0	mg/l
Half rate oxygen concentration	2	mg/l
Min. aqueous phase substr. conc. for biodecay	0	mg/l
Min. solid phase substr. conc. for biodecay	0	mg/gm
Half rate aqueous phase substr. conc. for biodecay	3	mg/l
Half rate solid phase substr. conc. for biodecay	4	mg/gm
Aqueous phase max. biogrowth rate	0.05	day^{-1}
Solid phase max. biogrowth rate	0.01	1/day
True yield coefficient	0.5	gm/gm
Oxygen/substr. coefficient	0.5	gm/gm
Death rate for active biomass	0.001	day^{-1}
Bulk density of adsorptive medium	1.2	gm/cm^3
Porosity of adsorptive medium	0.4	
Interstitial velocity	1	m/day
Dispersion coefficient for substrate	3	m^2/day
Dispersion coefficient for oxygen	2	m^2/day
Initial aqueous phase substr. conc.	1	mg/l
Initial solid phase substr. conc.	0	mg/gm
Initial oxygen conc.	0.6	mg/l
Initial biomass conc.	1.0	mg/l
Boundary type	constant flux	
Left boundary substr. conc.	20	mg/l
effective time	0-50	day
Left boundary oxygen conc.	5.0	mg/l
effective time	0-50	day
Biomass/medium conversion factor	1.0	

Table II. Input Parameters for Secondary Substrate

OPTIONS

Advection (yes)
Dispersion (yes)
Adsorption (yes, linear, equilibrium)
Biodecay (yes, Aerobic, first order)

PARAMETERS

Linear adsorption coeff.	0.05	cm^3/gm
Stage 1 1st order aqueous biodecay coeff.	0.02	day^{-1}
Stage 2 1st order aqueous biodecay coeff.	0.02	day^{-1}
Breakpoint primary substrate conc.	3	mg/l
Stage 1 1st order solid phase biodecay coeff.	0.01	mg/l
Stage 2 1st order solid phase biodecay coeff.	0.01	mg/l
Breakpoint primary solid phase conc.	0.01	mg/gm
Dispersion Coefficient for substrate	2	m^2/day
Initial aqueous phase substr. conc.	0.1	mg/l
Initial solid phase substr. conc.	0	mg/gm
Boundary type	constant conc.	
Left boundary substr. conc.	1	mg/l
effective time	0-100	day

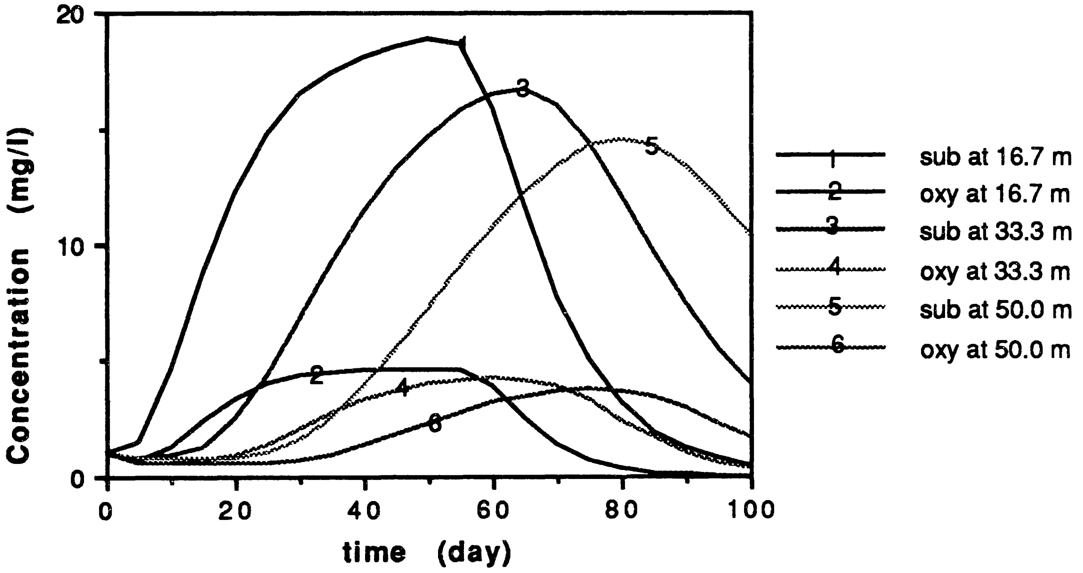


Figure 5. Breakthrough Curves for Primary Substrate and Oxygen

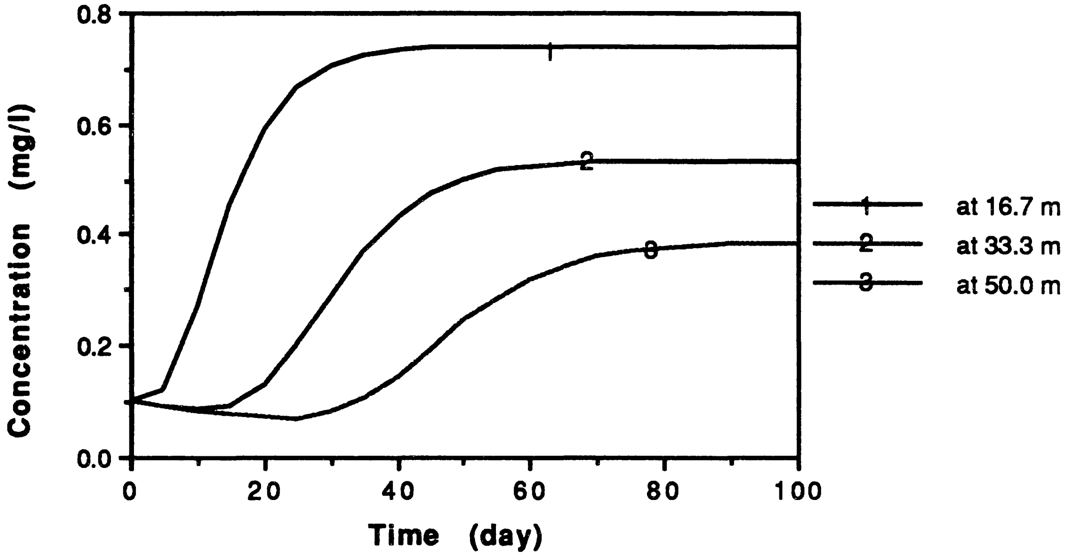


Figure 6. Breakthrough Curves for Secondary Substrate

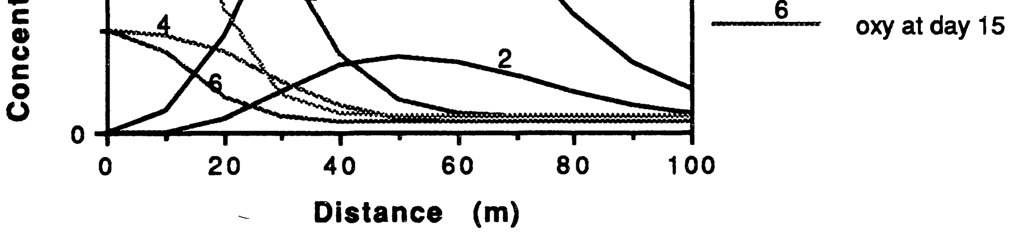


Figure 7. Profile Curves for Primary Substrate and Oxygen

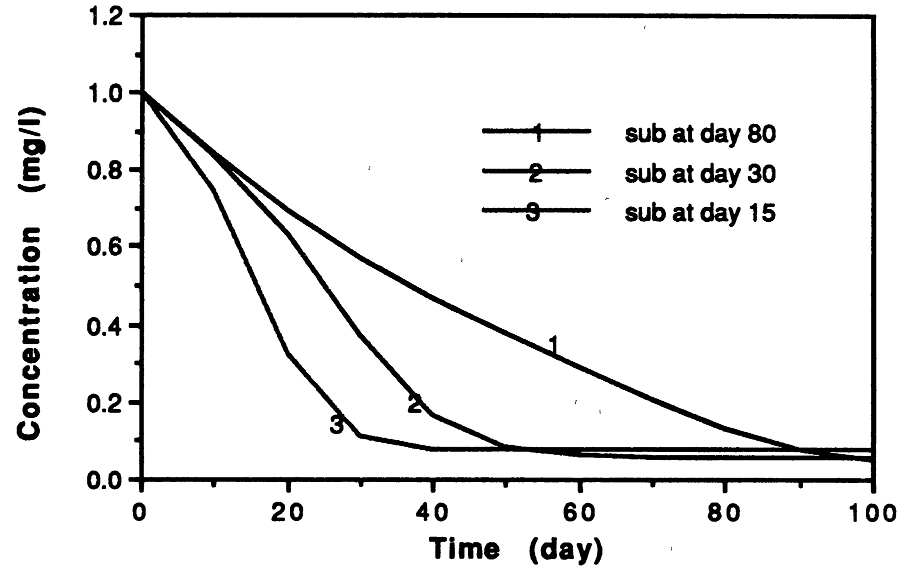


Figure 8. Profile Curves for Secondary Substrate

SUMMARY AND CONCLUSIONS

Although numerous groundwater solute transport models have been developed, only a few of them were developed as software for general use. Among those, it was felt, that improvements in two general areas were needed: 1) a more appropriate approach to incorporate the mechanisms of adsorption and biodecay processes. 2) the capability to simulate transport under different conditions and assumptions, as deemed appropriate by the user. In an attempt to accomplish these goals, a user friendly finite difference transport model was developed. As this was developed initially in one dimension, a proof of concept approach was pursued.

In addition to the conventional advective-dispersive transport, the model simultaneously simulates various adsorption and biodecay functions, including solid phase biodecay and secondary substrate utilization. Equilibrium or non-equilibrium adsorption for linear, Langmuir, or Freundlich isotherms can be selected from the model to accommodate different adsorptive properties. Aerobic and/or anaerobic biological decay in both aqueous and solid phases can be simulated independently or sequentially, using first order or Monod functions, and may be linked to the transport and consumption of oxygen. The growth of biomass is simulated by linking the stoichiometric yield and decay coefficients to substrate utilization. Boundary conditions for constant concentration or mass flux can be selected to suit practical problems.

For the functions discussed above, the user can easily select all or part of them by moving the highlighted cursor across the menu screen. This feature enables the user to evaluate and compare the transport under various conditions in a convenient way. Parameters can be input line by line within the model or called from a separate file. The input data can be viewed, modified and saved before actual simulation. The output is visually displayed on the screen as breakthrough and profile curves while also being saved in an ASCII file for later viewing or printing. The model is generally self-explanatory in excution with ample on-screen instruction. These features significantly improve the efficiency of the model over previous approaches. The level of interaction and control built into the model should raise the user's interest.

NOMENCLATURE

A = Mass lost due to adsorption, $ML^{-3}T^{-1}$

A_c = Mass accumulation rate , $ML^{-3}T^{-1}$

a = Constant for k_d correlation, dimensionless

A_s = Specific area of adsorptive medium, L^{-1}

B = Mass lost due to biodecay, $ML^{-3}T^{-1}$

b = Constant for k_d correlation, dimensionless

C = Aqueous phase substrate concentration, ML^{-3}

C_{min} = Minimum substrate concentration for aerobic biodecay, ML^{-3}

C_o = Solute concentration in water, for k_d correlation, ML^{-3}

C_L = Solute concentration at left fictitious node, ML^{-3}

C_p = Primary substrate concentration, ML^{-3}

C_{po} = Dividing primary concentration for secondary utilization, ML^{-3}

C_w = Solute concentration in octanol, for k_d correlation, ML^{-3}

D = Dispersion coefficient for substrate, L^2T^{-1}

De = Death of biomass, ML^{-3}

d_e = Death rate of active biomass, T^{-1}

$F(C,O)$ = Biological decay function, $ML^{-3}\ T^{-1}$

f = Mass of oxygen consumed/mass of substrate, dimensionless

f_a = Ratio of maximum adsorption capacity of biomass to aquifer material, dimensionless

f_{oc} = Soil organic content, %

Gr = True growth of biomass, ML^{-3}

J_{in} = Substrate mass flux coming to the segment, $ML^{-2}T^{-1}$

J_{out} = Substrate flux leaving the segment, $ML^{-2}T^{-1}$

k = Freundlich isotherm coefficient

k_1 = First order biodecay coefficient, T^{-1}

k_{21} = Biodecay coefficient for secondary substrate when $C_p > C_{po}$, T^{-1}

k_{22} = Biodecay coefficient for secondary substrate when $C_p \leq C_{po}$, T^{-1}

k_d = Solute solid/aqueous distribution coefficient, L^3M^{-3}

k_h = Half rate substrate concentration, ML^{-3}

k_L = Langmuir adsorption constant, L^3M^{-3}

kn_h = Half rate concentration for anaerobic biodecay, ML^{-3}

kn_{max} = Maximum anaerobic biodecay rate, $ML^{-3}T^{-1}$

kns_h = Half rate solid phase concentration for anaerobic biodecay, dimensionless

kns_{max} = Maximum solid phase anaerobic biodecay rate, T^{-1}

k_o = Half rate oxygen concentration, ML^{-3}

k_{oc} = Soil organic coefficient, dimensionless

k_{ow} = Octanol/water distribution coefficient for solute, dimensionless

k_q = Half rate solid phase concentration for aerobic decay, ML^{-3}

k_s = Internal mass transfer coefficient, LT^{-1}

ks_1 = First order solid phase decay coefficient, T^{-1}

M = Active biomass concentration, ML^{-3}

m_x = Mass of adsorbed solute, M

m = Mass of adsorptive medium, M

n = Exponential of Freundlich adsorption isotherm

O = Aqueous phase oxygen concentration, ML^{-3}

q = Solid phase substrate concentration, dimensionless

q_{min} = Minimum solid phase concentration for aerobic biodecay, dimensionless

Q = Maximum adsorption capacity, mass of adsorbate/mass of adsorbent

q^* = Equilibrated solid phase substrate concentration, dimensionless

R = Overall mass transfer coefficient for adsorption, T^{-1}

S = Cross section area of column, L^2

t = Time, T

U = Interstitial velocity, LT^{-1}

u = Specific biological growth rate, T^{-1}

u_{max} = Maximum specific biological growth rate, T^{-1}

us_{max} = Maximum specific biological growth rate for solid phase biodecay, T^{-1}

x = Distance, L

y_g = Growth yield coefficient, mass of biomass generated per mass of substrate decayed, dimensionless

ε = Porosity of adsorptive medium, dimensionless

ρ_b = Bulk density of the adsorptive medium, ML^{-3}

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CHAPTER II

A PRELIMINARY EVALUATION OF MODEL UNCERTAINTY GIVEN PARAMETER SENSITIVITY FOR SELECT TRANSPORT CODES

A PRELIMINARY EVALUATION OF MODEL UNCERTAINTY GIVEN PARAMETER SENSITIVITY FOR SELECT TRANSPORT CODES

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ABSTRACT

Preliminary sensitivity and uncertainty analyses were performed to examine the effects of adsorption model and parameter selection on the groundwater transport process. The effects of parameter uncertainty and model selection were analyzed in conjunction with different boundary input conditions. As expected, it was found that the retardation factor generally postponed arrival of the contaminant for the continuous boundary input conditions but did not attenuate the final concentration. Pulse boundary input conditions, however, not only postponed the arrival of contaminant but also reduced the peak concentration. For non-equilibrium adsorption, a smaller overall mass transfer coefficient (r) tended to have a slower but longer adsorption effect, compared to a larger value. As a result, breakthrough curves with a smaller r's showed a higher liquid phase concentration in the earlier time periods, and lower concentrations in later periods, compared to the breakthrough curves developed from larger mass transfer coefficients, or from equilibrium assumptions. While the sensitivity for r may be relatively small compared to that for the retardation factor, the overall effect on output concentration was still considerable when the wide range of possible values was considered.

The analyses also showed that local sensitivity maximums existed for specific r values, which would make first order uncertainty analysis unsuitable for this situation. Comparisons between equilibrium and non-equilibrium models showed that in the period $0 < T \leq R$ equilibrium assumptions always under estimated the concentration predicted by non-equilibrium models. A maximum error of -100% was possible given parameter selection. For the period of $R < T \leq 2R$, the equilibrium assumption may either under or over estimate the output concentration, with a maximum possible negative error of -50% and positive error of 25%. After T

> 2R, the equilibrium assumption always over estimated the concentration generated by non-equilibrium analysis, with a maximum error of 25%. Specifically, the mean error was less than 5% when the overall mass transfer coefficient was greater than 0.002 and 0.007/day for continuous and pulse boundary input, respectively, but a rapid increase in error was observed for both boundary conditions when the values of mass transfer coefficient decreased.

The results of model uncertainty analysis suggested that the indiscriminate use of linear equilibrium models may cause significant errors, especially when slow mass transfer dominates the adsorption process. An alternative non-equilibrium approach seemed necessary in this situation. This finding encourages future research work in the area of understanding adsorption kinetics in groundwater systems and in determining the mass transfer coefficients for a variety of marginally hydrophilic compounds.

INTRODUCTION

Recent developments in groundwater transport modeling have been aided by a combination of an increased understanding of fundamental transport mechanisms as well as the increasing availability of computers. Groundwater transport models have been routinely used by regulatory agencies and consulting firms to address management issues and assist in decision making. However, this ever increasing use of models has raised concerns as to uncertainties associated with their abilities to simulate real world pollution problems. These uncertainties have become an additional important factor in performing risk assessments for groundwater contamination problems (Haimes, 1984). Accurate simulation depends upon such factors as the appropriate description of pertinent transport mechanisms, the proper choice of transport codes and the use of accurate input parameters.

Two types of uncertainties may impact the simulation process: those associated with model selection and those related to parameter identification. Model uncertainty results from the improper description of the transport mechanisms, or by applying the model to situations unwarranted by its formulation. Parameter uncertainty occurs when inaccurate or improper input values are used. Model and parameter uncertainties have been classified as type I and type II errors respectively (Burges *et al*, 1975), and both have been shown to affect the reliability of the simulation.

For groundwater contaminant transport problems, these uncertainties tend to become more obvious when complex transport mechanisms are involved and are exacerbated by the difficulties in obtaining accurate and consistent input data. The discrepancies between the prediction and underlying monitoring data due to improper model selection or to uncertain input data can make the results unusable. Villeneuve *et al* (1988) found that for the unsaturated zone transport model, PRZM, a variation of 15-22% in the degradation constant, or a 24% variation in the adsorption constant, could lead to 100% uncertainty of the output pesticide concentration

Recently, uncertainty analysis has become a major research topic and a considerable amount of work has been published. Burges *et al* (1975) first applied basic uncertainty theory to stream water quality evaluations. Subsequent applications have also been found in groundwater determinations. Loague *et al* (1990) assessed the impact of uncertainty in soil, meteorological and chemical properties on pesticide leaching. Medina *et al* (1989) employed sensitivity and Monte Carlo techniques to analyze the uncertainties associated with the impact of waste sites on groundwater quality, while Villeneuve *et al* (1988) investigated parameter sensitivity for the unsaturated root zone model (PRZM). While these efforts primarily employed first order or Monte Carlo methods to analyze parameter uncertainty, model uncertainty has attracted less attention. This paper attempts a preliminary assessment in this area within the context of parameter selection. This work primarily focused on the sensitivity of different parameters and the possible errors resulting from model selection. Specifically, the interactions between equilibrium and non-equilibrium linear adsorption with attendant parameter selection were investigated.

The deterministic model used for these purposes was developed by Chen and McTernan (1991). This Multi-substrate, Multi-option Groundwater Transport Model (MMGTM) consists of various sub-models and can simulate the transport of two substrates and oxygen under various conditions including advection, dispersion, adsorption, and biological decay. Adsorption and biological decay options available to the user include equilibrium or non-equilibrium adsorption with Linear, Langmuir or Freundlich isotherms as well as Monod or first order biological decay.

The mass balance equation for solute transport under advection, dispersion and adsorption can be expressed as the following equation.

$$\frac{\partial C}{\partial t} = -U\frac{\partial C}{\partial x} + D\frac{\partial^2 C}{\partial x^2} - \frac{\rho b}{\varepsilon}\frac{\partial q}{\partial t} \qquad (1)$$

Where adsorption is expressed as the last term of the equation. Aquifer materials, including minerals, organics, and microorganisms, can provide adsorptive surfaces for contaminants in groundwater. The extent of adsorption depends upon the affinity between the contaminants and these aquifer materials. As a result of adsorption, the contaminant mass in the liquid will be attenuated during the transport process. The distribution of solute between liquid and solid phases is commonly described by the Linear isotherm which has the form:

$$q = \frac{m_x}{m} = k_d C \qquad (2)$$

and indicates that solute concentration in the solid phase is proportional to the concentration in the liquid phase. The adsorption of a number of organics onto soil at low concentration has been reported to be linear (Means *et al*, 1980, Hassett *et al*, 1980) and served as a starting point for this analysis.

Applying the differential train rule and combining with Equation 2:

$$\frac{\partial q}{\partial t} = \frac{\partial q}{\partial C}\frac{\partial C}{\partial t} \qquad (3)$$

$$\frac{\partial q}{\partial C} = K_d \qquad (4)$$

and substituting Equations 3 and 4 into equation 1:

$$R\frac{\partial C}{\partial t} = -U\frac{\partial C}{\partial x} + D\frac{\partial^2 C}{\partial x^2} \qquad (5)$$

Where

$$R = 1 + \frac{\rho b\, K_d}{\varepsilon} \qquad (6)$$

R is also known as retardation factor, and is interchangeable with K_d for a given bulk density and porosity of the adsorbent.

The above process assumes an *equilibrium* always exists between the liquid and solid phases, and is defined by Equation 4. This assumption is valid only if the transfer of mass from liquid phase to the solid is instantaneous. Adsorption, in fact is a time dependent mass transfer process where the equilibrium assumption may be used only if the mass transfer rate is fast relative to the groundwater velocity. Many current groundwater transport codes employ equilibrium or retardance approaches to simulate contaminant transport and a great deal of work has focused on determination of Kd or retardation factor. Several methods have been developed for the determination of these values, including lab batch adsorption tests, field tracer measurements as well as soil organic content correlations. However, all of these efforts have been based upon the linear, equilibrium assumption. While acceptable in some circumstances, this has been shown to be deficient in others (Freeze and Cherry, 1979; Chen *et al,* 1991). Selection of a retardation based approach to simulate these types of conditions will introduce much uncertainty and resultant error in the final output.

If the mass transfer process is slow, however, an equilibrium assumption may become inappropriate and a kinetically based approach is more fundamentally valid. Such conditions could occur with specific hydrophilic chemicals or when hydraulic conditions are altered during remediation. One approach to describe this process is by the internal resistance model, provided by Hines and Maddox (1985):

$$\frac{\partial q}{\partial t} = k_S A_S (q^* - q) \tag{7}$$

Here an overall mass transfer coefficient, r, may be used to represent K_S and A_S:

$$r = k_s A_s \tag{8}$$

Equation 7 becomes:

$$\frac{\partial q}{\partial t} = r (q^* - q) \tag{9}$$

Substitution into Equation 1 yields:

$$\frac{\partial C}{\partial t} = -U \frac{\partial C}{\partial x} + D \frac{\partial^2 C}{\partial x^2} - \frac{\rho b}{\varepsilon} r (q^* - q) \tag{10}$$

Particular to adsorption, model uncertainty results from the selection of either equilibrium or non-equilibrium algorithms while parameter uncertainty in selecting either the distribution coefficient K_d or an overall mass transfer coefficient r can also reduce accuracy. The variation in K_d may come from many sources: the heterogeneity of the aquifer materials, the uneven distribution of organic materials, variation in temperature, error from field and lab measurements or from regression models used to correlate chemical and geological data. In addition to these factors, the surface area of aquifer materials and the groundwater velocity also have important impacts on the overall mass transfer coefficient r. This paper investigated the impact of variability of parameters K_d and r on the model output, as well as their effects on the model uncertainty.

METHODOLOGY

Data Transformation

While each input and output parameter in MMGTM is fully dimensioned, some data were normalized and transformed to facilitate the analysis.

Dimensionless time — The time scale in breakthrough curves used in this analysis was rendered dimensionless by defining the ratio of actual time to the time needed for the groundwater to travel from the boundary to the specified spatial node under the given groundwater velocity. For example, with a velocity equal to 0.2 m/d, and the spatial node located 100 m from the boundary, 500 days were needed to reach the node. Dimensionless time became 0.8 for an actual time of 400 days, taking into account actual time, groundwater velocity, and the distance from the boundary to the spatial node. Dimensionless time represented a set of physical conditions rather than a single representation of time and was chosen for more generic evaluation in that velocity components could be reduced to pore volumes or retardance reciprocals allowing extrapolation of the results to other conditions.

Dimensionless Concentration — Dimensionless concentration was defined as the ratio of actual solute concentration to the possible maximum concentration for the entire simulation period. For the continuous constant boundary concentration, the maximum concentration was equal to the boundary concentration. For pulse constant boundary concentration, the maximum concentration varied with the duration of the input time and other physical properties but was always less than the boundary concentration, the difference being storage in the element.

Imaginary Distribution Coefficient and Retardation Factor

For non-equilibrium adsorption, the distribution coefficient K_d describing equilibrium conditions was not appropriate, as the molecular distribution between the aqueous and solid phases defined by equilibrium was not achieved. To address this, an imaginary distribution coefficient, K_i, could be defined as a reference state for a quasi-equilibrium adsorption level, assuming no mass transfer resistances would exist. In the simulation process, Ki defines the reference solid phase concentration q*, which determined the overall mass transfer rate (Equation 9). Similarly, a corresponding imaginary retardation factor R_i, was calculated by Equation 6.

Input Data

To isolate adsorptive effects for evaluation, the following physical properties were fixed throughout the analysis: groundwater velocity, dispersion coefficient, bulk density and the porosity of aquifer materials. While it is recognized that these data may vary significantly from aquifer to aquifer, they were fixed for this effort to minimize extraneous variation beyond that introduced by the selection of either the adsorption model or from the pertinent parameters. The use of dimensionless time within the aquifer volume allowed these to be treated as constants. Data from other conditions can be compared to the results from this investigation when corrected to a similar framework.

Two types of boundary conditions, continuous and pulsed input, were employed, while the boundary concentration for this analysis was fixed at 0.2 mg/l. For the continuous conditions, the boundary concentration was effective throughout the entire simulation period, while its effective duration was 100 days for the pulsed input conditions.

The distribution coefficient, K_d, and the overall mass transfer coefficient r were varied in the sensitivity analysis with values for K_d ranging from zero (no adsorption) to 1.1 cm^3/gm, with a corresponding range of retardation factor from 1 to 4.3. This K_d range was selected to address typical values for a number of pesticides and halogenated organics in soil and aquifer materials (Siegrist and McCarty, 1987; Zhong *et al*, 1986). The range of overall mass transfer coefficients chosen for this analysis was from zero to a value that resulted in an equivalent equilibrium condition, where further increase of the value did not change the resultant output. A summary of input data used in this analysis is shown in Table 1.

Table 1. Input Parameters Used in Analysis

Parameters	Values
Interstitial velocity	0.2 m/day
Dispersion coefficient	0.4 m^2/day
Bulk density of aquifer materials	1.2 gm/cm^3
Porosity of aquifer materials	0.4
Adsorption distribution coefficient	0 - 1.3 cm^3/gm
Retardation factor (corresponding to K_d)	1 - 5
Overall mass transfer coefficient	0 - ∞

Sensitivity Analysis

Sensitivity analysis deals with the response of change of model output to the change of input parameters. The coefficient of sensitivity S has been expressed previously by Sykes *et al* (1985) as:

$$S = \frac{\partial P/P}{\partial \alpha/\alpha} \qquad (11)$$

which reflects the percent change in output values given the percent change of input data. The sensitivity of a parameter depended upon the magnitude as well as the sign of the coefficient. While the magnitude indicated how sensitive the output was to the change of input, the sign determined the direction of the change. A positive sign indicated that the output concentration increased with an increasing input value, while a negative sign indicated that the concentration decreased with an increase in input value.

A finite difference form of Equation 11 was used in the analyses to compute the coefficient of sensitivity. For most applications the relationship between input and output is not linear and the magnitude as well as the sign of the coefficient may vary for different values of input data. For this reason, the evaluation of sensitivity coefficients covering a range of input values was necessary.

Analysis of Mean Error

The difference between two breakthrough curves resulting from equilibrium and non-equilibrium models respectively was compared to determine the mean error resulting from application of an equilibrium model when a non-equilibrium situation dominated. The length of time being analyzed for the respective curves was divided evenly into 20 intervals. At each interval the square of the difference between the normalized concentrations for equilibrium and non-equilibrium conditions was calculated. The sum of the square was then divided by 20 to get the mean square. The mean error is the square root of this mean square. The formula used for the calculation was:

$$Em = \sqrt{\frac{\sum_{i=1}^{20}(Ce_i - Cn_i)^2}{20}} \qquad (12)$$

E_m reflects relative difference between the results from two different models over the period of evaluation.

RESULTS

Effects of retardation factor

The equilibrium breakthrough curves for different retardation factors are shown in Figures 1 and 2, for continuous and pulse boundary input respectively. The concentration and time in these figures have been normalized to dimensionless scales.

Each equilibrium breakthrough curve for continuous boundary input was symmetrical with a final concentration approaching one. As expected, with increasing retardance the curves eventually showed reduced breakthrough and

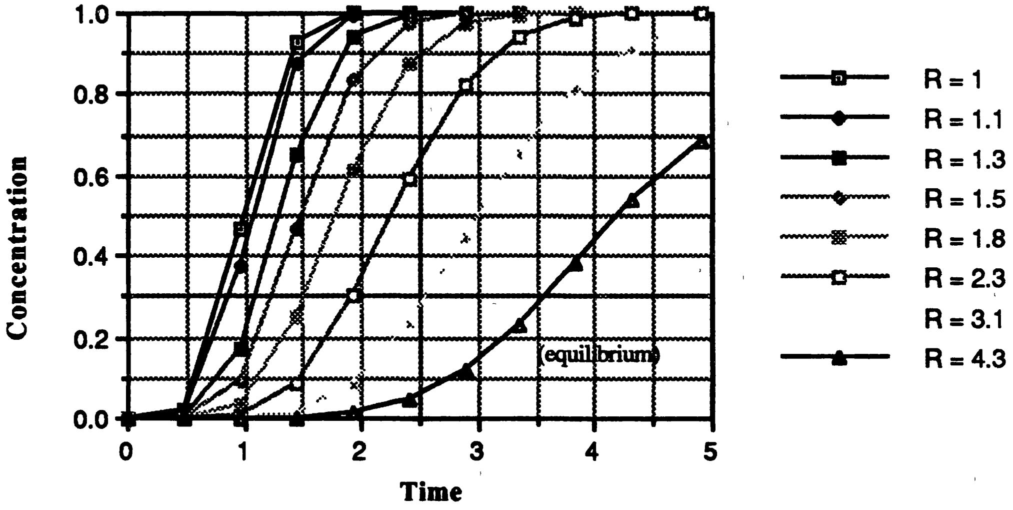

Figure 1. Effect of Retardation on Breakthrough Curves (Continuous Boundary Input)

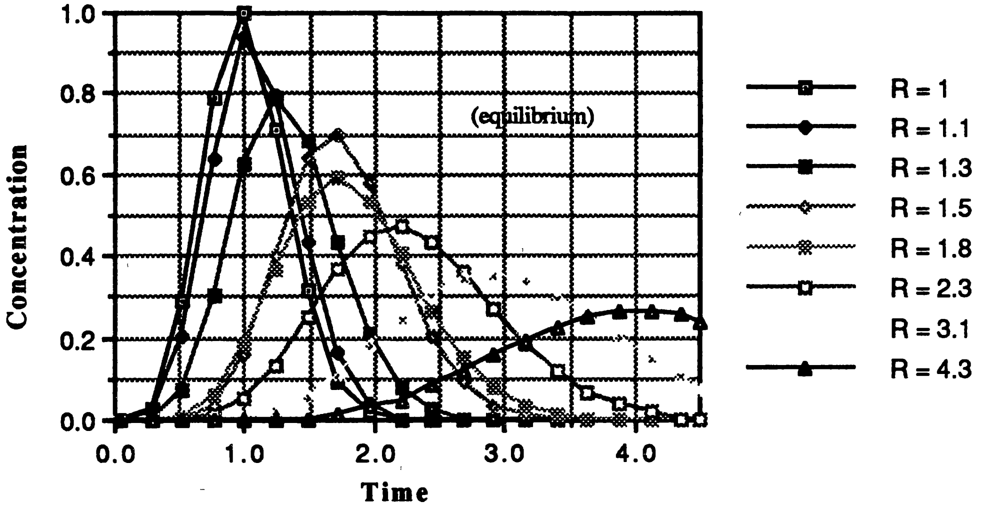

Figure 2. Effect of Retardation on Breakthrough Curves (Pulse Boundary Input)

greater storage within the volume. It was also noted that for each curve, the time corresponding to a relative concentration of 0.5 was always equal to the value of retardation factor. For the pulsed boundary input, the curves exhibited a symmetrical "bell" shape. As with the continuous boundary, increased retardance increased the time of plume passage. The time of peak appearance was equal to the corresponding value of retardation factor R.

Effects of Overall Mass Transfer Coefficient

The breakthrough curves under non-equilibrium adsorption are given in Figures 3 through 6. Figure 3 illustrates the effect of mass transfer coefficient selection at an imaginary retardation factor of 2.2, for continuous boundary input. Figure 4 shows a similar effect as Figure 3 but at a greater retardation ($R_i = 3.4$) while Figures 5 and 6 show the effect of non-equilibrium adsorption for pulsed boundary input condition for these same values of R_i.

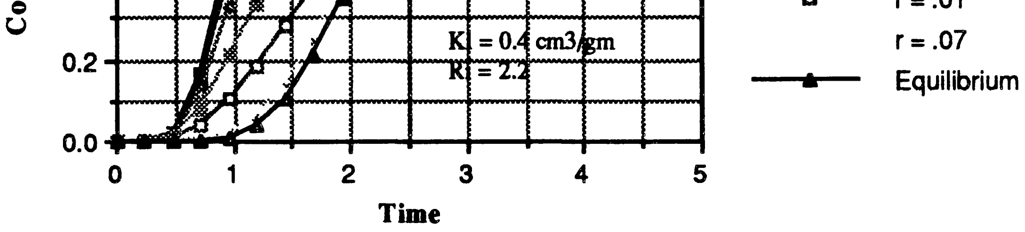

Figure 3. Effect of Mass Transfer Coefficient on Breakthrough Curves (Continuous Boundary Input, $R_i = 2.2$)

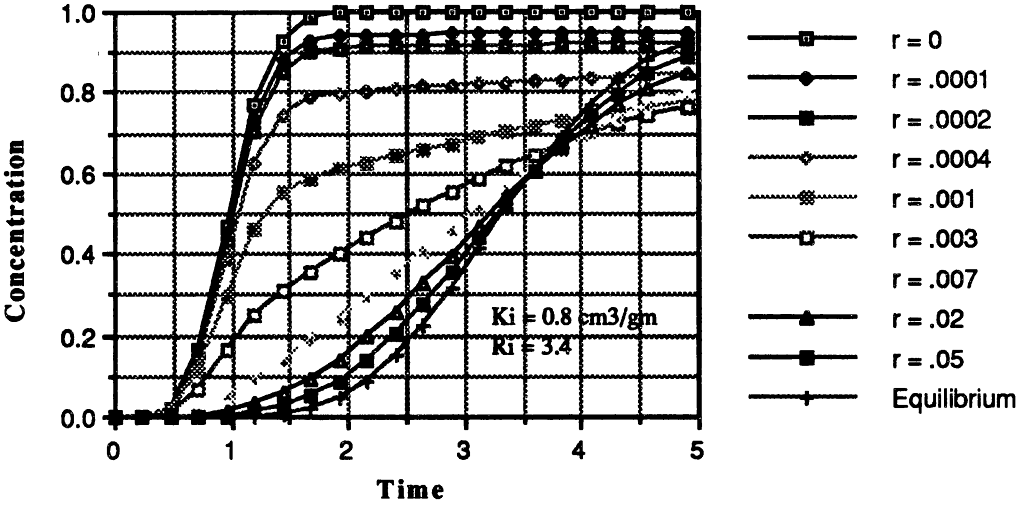

Figure 4. Effect of Mass Transfer Coefficient on Breakthrough Curves (Continuous Boundary Input, $R_i = 4.3$)

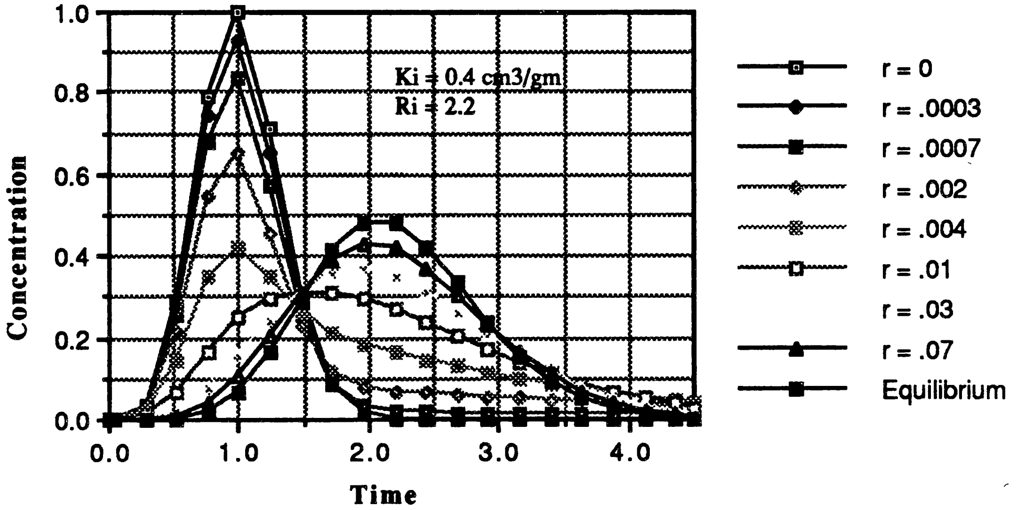

Figure 5. Effect of Mass Transfer Coefficient on Breakthrough Curves (Pulse Boundary Input, $R_i = 2.2$)

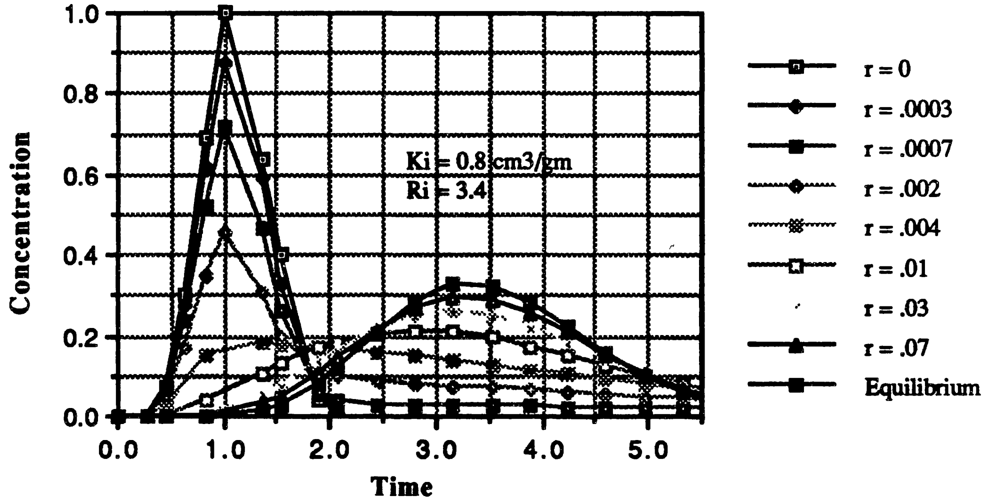

Figure 6. Effect of Mass Transfer Coefficient on Breakthrough Curves (Pulse Boundary Input, R_i = 3.4)

The comparison of non-equilibrium and equilibrium breakthrough curves with equivalent K_i or R_i can be seen in Figure 3. When the mass transfer coefficient was equal to zero, the breakthrough curve overlapped the curve resulting from the no-adsorption option (i.e. advective-dispersive). As the magnitude of the mass transfer coefficient increased, the breakthrough curve tended to approach the curve resulting from equilibrium adsorption with equal K_d or R values. Selection of either zero or a large mass transfer coefficient resulted in a 100% breakthrough of concentration with increased time. However, asymmetrical curves with prolonged, less than total breakthrough tails were observed for an intermediate range of r. The equilibrium assumption may either over or under estimate the simulated concentration, depending upon the time at which the concentration was observed. Figure 4 presents similar comparisons for a larger R_i. The greater R_i transferred the equilibrium curve farther along the temporal axis, while the curve for r equal to zero overlapped that from no adsorption, as with the previous case. Zero mass transfer reduces transport to the advective-dispersive portion of equation 1, while at higher mass transfer coefficient values, equilibrium is approximated.

Figure 5 shows the effect of mass transfer coefficient selection on breakthrough curves under non-equilibrium, pulsed boundary input conditions. As with the continuous boundary examples, the breakthrough curve for r equal to zero coincided with the advective-dispersive case. As r increased, the concentration peaks decreased and appeared at increased time until r reached 0.011. As r further increased, the peak began to increase and approached equilibrium adsorption. The breakthrough curves for no or equilibrium adsorption were symmetrically shaped with zero concentration at both ends. However, asymmetrical breakthrough curves with non-zero concentration tails were observed for non-equilibrium adsorption over a range of mass transfer coefficients. Figure 6 illustrated the similar effect with a larger value of R_i ($R_i = 3.4$). In this situation, the curve for r equal to zero again overlapped the advective-dispersive condition, as with in Figure 5.

Sensitivity of Retardation Factor and Mass Transfer Coefficient

Sensitivity analysis was applyed to the retardation factor and overall mass transfer coefficient for equilibrium and non-equilibrium conditions respectively. Figure 7 presents the sensitivity for retardation factor R in an equilibrium situation. For any value of retardation factor, the sensitivity was always negative, indicating that the solute concentration, as expected, would decrease as R increased. The magnitude of sensitivity increased as R increased, indicating that selection of higher values of R resulted in greater sensitivity. Although Figure 7 was generated at time equal to 1.6, the general effect was similar at other times. This can be observed by examining the breakthrough curves in Figure 1.

The sensitivity of output concentration to the overall mass transfer coefficient showed different patterns in two time ranges ($T < R$ and $T > R$), as indicated in

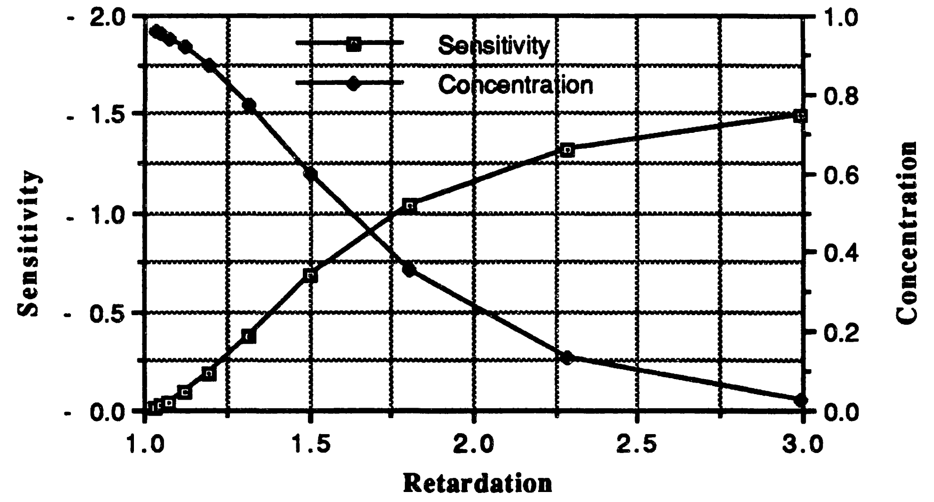

Figure 7. Sensitivity and Output Concentration as a Function of Retardation Factor (at T = 1.6).

Figures 8 and 9. Data presented in Figure 8 showed that the sensitivity was always negative for any value of mass transfer coefficient, indicating that output concentration always decreased with the increased R values. The concentration dropped from 1 to 0.56 as r increased from 0 to 0.1/day. The magnitude of sensitivity, however, exhibited a different pattern as r increased. A maximum negative sensitivity value occurred at about r equal to 0.001 day^{-1}, and the magnitude of sensitivity decreased as r deviated from 0.001, approaching zero in both directions.

A typical curve representing time T > R is illustrated in Figure 9. In this case not only the magnitude of sensitivity varied with r, but the sign also changed. Two sensitivity peaks were generated, one positive and the other negative. The opposite signs indicated different directions of response of output concentration to the input parameter. The concentration curve in the figure showed that as r increased over the range 0.0001 to 0.00105, the output concentration decreased from 0.97 to 0.88. But as r continued to increase from 0.00105 the breakthrough concentration began to

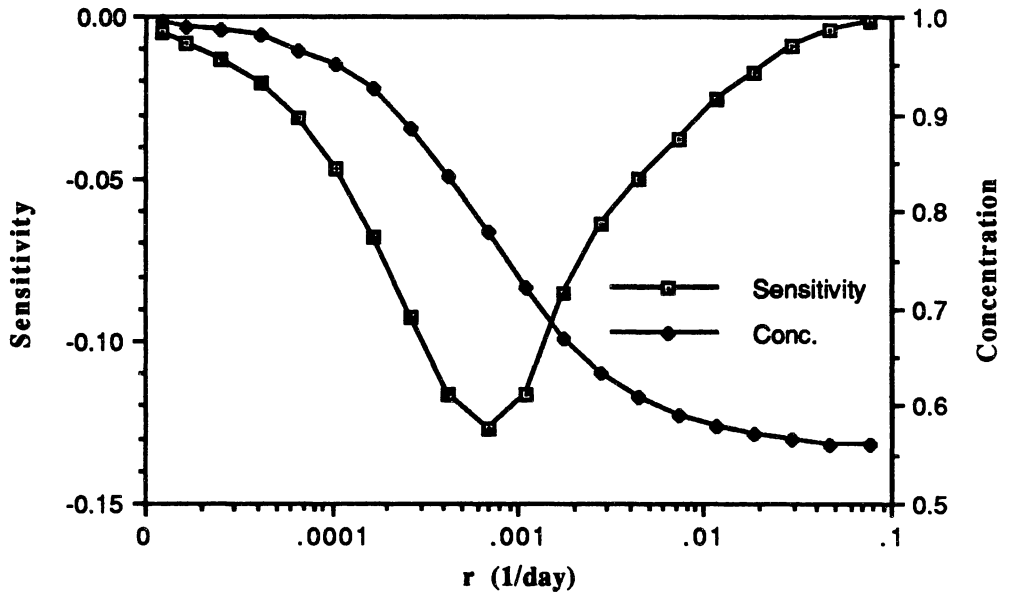

Figure 8. Sensitivity and Output Concentration as a Function of Mass Transfer Coefficient (Continuous Boundary Input, T = 0.94 R)

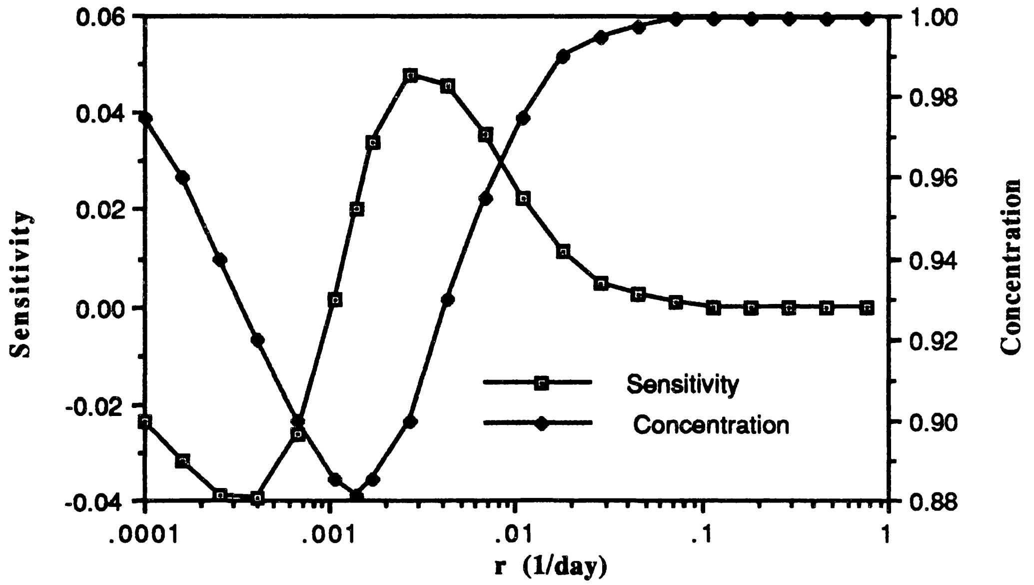

Figure 9. Sensitivity and Output Concentration as a Function of Mass Transfer Coefficient (Continuous Boundary Input, T = 2.2 R)

increase and approached 1 when r equaled 0.1. Accompanying sensitivity cycled from maximum negative values through peak positive response to asymptote to approximate zero above r = 0.1.

Uncertainties for Parameters and Models

The possible errors introduced by applying an equilibrium model to non-equilibrium situations are presented in Figure 10, where the error in ordinate represents the difference between the concentrations predicted from equilibrium and non-equilibrium models, respectively. Time was expressed as multiples of the retardation factor. To locate the specific time, a conversion of time into the multiple should be performed. For example, for a retardation factor of 2.0, a dimensionless time of 3.0 had a multiple of 3.0/2.0 = 1.5. The error corresponding to 1.5R in Figure 10 was the error for T = 3.0. A positive error implied that the simulated equilibrium concentration was greater than the concentrations from non-equilibrium applications while a negative sign represented the contrary. Values along the abscissa represent dimensionless time (expressed in terms of retardation factor) at which the error occurred. The shaded area in Figure 10 encompasses errors from the model selection for all possible values of the mass transfer coefficient. It can be seen that the magnitude as well as the signs of the possible errors varied significantly with detention time or pore volume. At any specific time, a range of error can be obtained from the figure. The specific error may be any value within this range, depending upon the magnitude of the mass transfer coefficient. The ultimate error must be evaluated on a case by case basis, but in the special case for r equal to infinity, the error would fall on the horizontal axis, indicating a zero error, or the equilibrium solution. As the time went beyond 3R, the possible error decreased slowly as time increased, approaching zero when the time tended to be infinite.

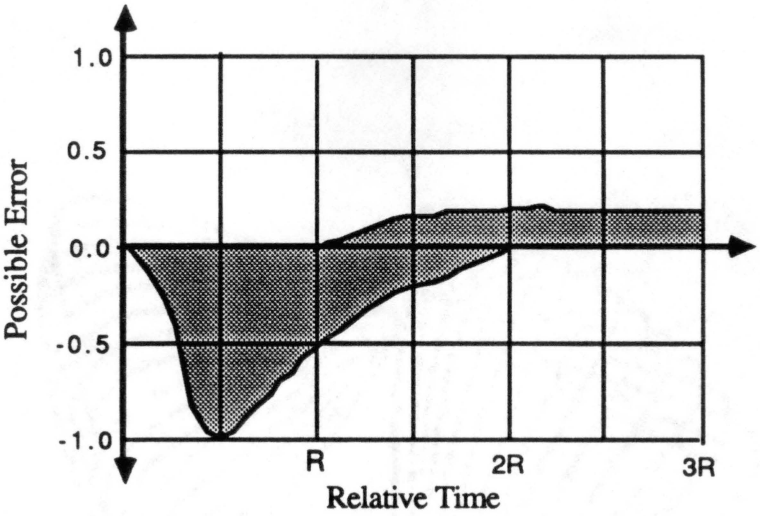

Figure 10. Possible Error Resulted from Assumption of Equilibrium Adsorption

Figures 11 and 12 present the mean errors expected if an equilibrium model was used to simulate non-equilibrium conditions over the time period of $0 \leq T \leq 2R$, for continuous and pulsed boundary conditions respectively. The results were calculated from equation 12 and give an estimate of the uncertainty over a time period rather than at a particular time. It can be seen that for both boundary conditions, the mean error increased rapidly as the value of mass transfer coefficient decreased. This would occur either at sites with low adsorptive materials and/or with hydrophilic solutes.

DISCUSSION

The selection of retardation factors caused a variation of contaminant arrival time and intermediate concentrations for the continuous boundary condition. It did not, however, attenuate the final concentration which was always equal to the boundary's value. For the pulsed boundary input, however, an over estimate of R not only resulted in a delayed arrival of contaminant but also generated a reduced peak concentration. When application to groundwater remediation practice is considered, the uncertainty in R may affect the prediction as to whether a maximum allowable

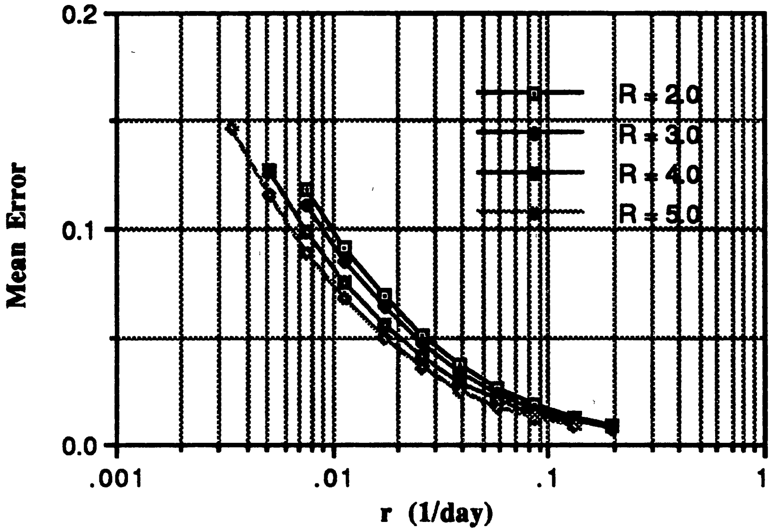

Figure 11. Mean error resulting from equilibrium assumption as a function of mass transfer coefficient (Continuous boundary input).

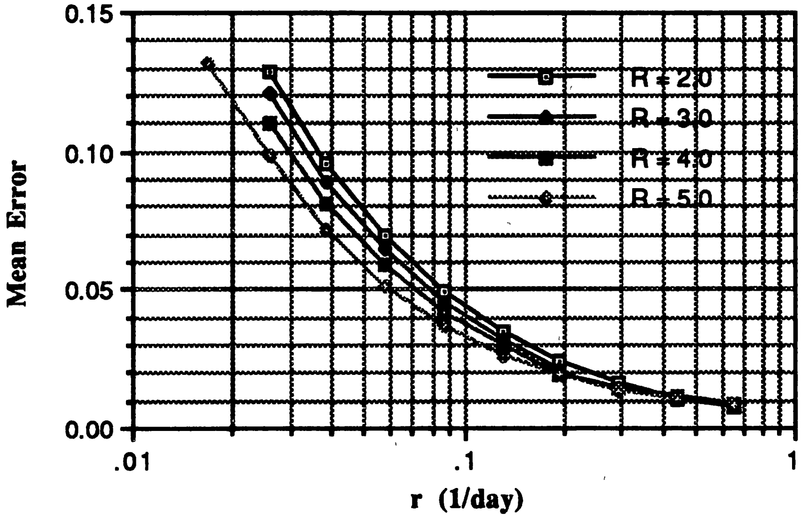

Figure 12. Mean error resulting from equilibrium assumption as a function of mass transfer coefficient (Pulse boundary input).

concentration would be violated and if so, when this violation would occur. The magnitude of uncertainty can be seen in Figure 7, where a maximum sensitivity coefficient of 1.5 was observed corresponding to R = 3.0. This value of sensitivity coefficient indicated that 66.7% uncertainty in R would result in 100% uncertainty in the predicted concentration. The increased sensitivity with increased R also indicated that an over estimated R posed not only a potential risk for under prediction of concentration but also resulted in greater uncertainty for the prediction.

The impact that selection of an overall mass transfer coefficient had on output exhibited different patterns for two time periods. An over estimated r would predict a lower concentration at earlier observation times and a higher concentration in later periods. This is explained by examination of Equation 9, where the overall mass transfer from liquid to solid is the product of the mass transfer coefficient r and the driving force represented by the difference between the equilibrium-based solid concentration q* and the actual solid concentration r(q*-q). Initially, when the driving force was relatively large due to a smaller q, the magnitude of r dominated or controlled the overall mass transfer process. A bigger r in this period resulted in more mass transfer from liquid to solid yielding a lower liquid phase concentration. In later time periods, however, the driving force became smaller due to previous adsorption, and began to control the overall mass transfer. A higher solid phase concentration occurred for larger r values as a result of more mass adsorbed from the previous period. Even taking into account the greater r, the overall mass transfer from the liquid to solid became weaker than in cases with a smaller r. This resulted in higher liquid phase concentration as mass continued to be transported from the boundary.

The magnitude and the distribution of uncertainty from the selection of a mass transfer coefficient differed from those from retardation factor. As shown in Figures 8 and 9, local maximum uncertainty peaks occurred for specific values of mass transfer coefficients, while the magnitude of uncertainty due to retardation increased continuously with R. This indicated that the uncertainty resulting from selection of an overall mass transfer coefficient was more difficult to determine than the corresponding equilibrium situation. The range of sensitivity resulting from the selection of a mass transfer coefficient was relatively smaller than that from identifying a value of retardance. However, due to the wide range of possible r values and less reliable methods for its determination, the overall uncertainty may still remain significant.

The evaluation of uncertainty from improper use of an equilibrium model for non-equilibrium situations can be preliminarily identified by employing Figure 10, with a simple transformation. For example, if one wants to estimate the error from the prediction of 400 day's concentration by improperly using an equilibrium model for non-equilibrium situations, the time should be first transformed to dimensionless units. Assuming a dimensionless time of 0.8 is obtained from given physical conditions, and the retardation used for the equilibrium simulation is 4.0, then the time expressed as multiple of retardation factor becomes 0.8/4.0 = 0.2R. Using this value in Figure (10), the error range is 0 to -0.4. This means for any possible value of mass transfer coefficient, the maximum error could not be greater than 40%. The actual error would fall between 0 to 40%, depending upon the value of mass transfer coefficient selected.

The above example gives an evaluation of model uncertainty at a specific time. However, uncertainty varied significantly for differing times. General patterns of the uncertainty can be evaluated over three time periods. In the period $T < R$, all possible errors were negative, indicating the equilibrium model always under predicted the actual concentration. A maximum 100% error appeared at $T = 0.5$ R, and relatively large errors occurred near this region. This indicated that the prediction of concentration around this time was more vulnerable to model selection. These relatively large errors and their direction (under estimating the actual value) in this time period present a potential risk when using the equilibrium model inappropriately.

In the time period T > 2R, the error became positive with a possible maximum value of 25%. In a practical sense, uncertainty in this period did not pose an environmental risk, as the resulting over prediction of contaminant concentration would generate conservative remediation designs or management choices. This would, of course, result in significant potential waste of resources.

In the period R < T < 2R, the range of the error was from +25% to -50%, depending upon the value of the mass transfer coefficient selected. Whether the equilibrium assumption over or under estimated the concentration could not be predetermined due to possible opposite signs.

Figure 10 could be used for an initial estimation of model uncertainty to determine whether the use of an equilibrium model would be acceptable, even if the mass transfer coefficient were unknown. For these situations where the value of mass transfer coefficient was known, or could be estimated within a range, an alternative estimate can be found in Figures 11 and 12. These figures were generated by using Equation 12 to analyze the difference between equilibrium and non-equilibrium breakthrough curves over a period of time equal to twice the value of retardation factor. This analysis, instead of generating the error at a specific time as provided in Figure 10, gives an average error over the time equal to 2R.

Given the same value of mass transfer coefficient, a slightly smaller error was observed for a greater value of retardation factor, but this effect appeared minimal. The main error was due to the selection of mass transfer coefficient. For a retardation factor of 2.0 and continuous boundary input condition, the error from improper use of the equilibrium model would be less than 5% if the overall mass transfer coefficient was greater than 0. 025/day. A larger error was observed for pulsed boundary input conditions, with the same retardation factor and mass transfer coefficient. In both continuous and pulsed boundary input conditions, a rapid increase in error occurred as the mass transfer coefficient decreased. The larger expected error associated with smaller mass transfer coefficient selection signified the inability of the equilibrium model to simulate non-equilibrium situations, especially when slow mass transfer dominated the adsorption process. These situations tended to occur when hydrophilic compounds were present and hydraulic contact time was limited. The results from Figures 11 and 12 can also be used for general error estimations for situations where the equilibrium model has been used to simulate non-equilibrium adsorption.

SUMMARY AND CONCLUSIONS

This study has investigated the uncertainties associated with parameter identification and model selection in relation to equilibrium and non-equilibrium adsorption. Transport models describing equilibrium and non-equilibrium adsorption with parameters describing retardation and mass transfer were included in the uncertainty analysis for both continuous and pulsed input boundary conditions. For the continuous boundary input condition, the uncertainty of the model prediction due to selection of retardation factor was found to affect mainly the contaminant's arrival time but not the concentration in extended time, which always approached the value at boundary. However, the selection of this parameter resulted in uncertainty in predicting the arrival time as well as the maximum concentration of contaminant for the pulsed boundary input condition.

While the sensitivity of the retardation factor showed similar results to other research work (Villeneuve *et al* ,1988), the sensitivity resulting from the selection of the mass transfer coefficient exhibited different and more complicated patterns. These included the local maximums of sensitivity for specific r values and sign changes at different observation times. These properties demonstrated a higher degree of uncertainty when non-equilibrium adsorption dominated.

This study has shown a considerable amount of uncertainty exists when selecting between equilibrium and non-equilibrium models when the rate of mass transfer is slow. As the selection of an appropriate model with proper parameters is an important step to achieve reliable simulation results, further research in the area of understanding adsorption kinetics in groundwater systems and determining the mass transfer coefficients for a variety of hydrophilic compounds seems necessary.

NOMENCLATURE

A_s = Specific area of adsorptive medium, L^{-1}

C = Aqueous phase substrate concentration, ML^{-3}

Ce = Normalized output substrate concentration for equilibrium adsorption, dimensionless

Cn = Normalized output substrate concentration for non-equilibrium adsorption, dimensionless

D = Dispersion coefficient for substrate, L^2T^{-1}

E_m = Mean error between equilibrium and non-equilibrium output concentrations for a period of time, dimensionless

k_d = Solute solid/aqueous distribution coefficient, L^3M^{-3}

k_i = Imaginary solute solid/aqueous distribution coefficient, L^3M^{-3} (for non-equilibrium adsorption process)

k_s = Internal mass transfer coefficient, LT^{-1}

m = Mass of adsorptive medium, M

m_x = Mass of adsorbed solute, M

P = Value of output data in sensitivity analysis

q = Solid phase substrate concentration, dimensionless

q* = Equilibrated solid phase substrate concentration, dimensionless

R = Retardation factor, dimensionless

r = Overall mass transfer coefficient for adsorption, T^{-1}

R_i = Imaginary retardation factor, dimensionless (for non-equilibrium adsorption process)

S = Coefficient of sensitivity, dimensionless.

T = dimensionless time, dimensionless.

t = Time, T

U = Interstitial groundwater velocity, LT^{-1}

x = Distance, L

α = Value of input data in sensitivity analysis

ε = Porosity of adsorptive medium, dimensionless

ρ_b = Bulk density of the adsorptive medium, ML^{-3}

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APPENDIX. MMGTM USER MANUAL

Multi-substrate, Multi-option Groundwater Transport Model

(version 1.1)

USER'S MANUAL

by

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1.GENERAL DESCRIPTION

Introduction

The Multi-Substrate, Multi-option Groundwater Transport Model (MMGTM) is a one-dimensional finite difference model developed to simulate the transport of groundwater contaminants under various physical, chemical and biological conditions. The code was written in Microsoft QuickBasic 4.0, and consists of about 6,000 lines in 12 separate modules. The size of the compiled program is about 300 K bytes.

Application

This program was developed mainly for proof of concept applications. It can also be used for educational purposes to demonstrate the effects on contaminant transport by various physical, chemical and biological conditions. It can also be used for actual simulation if the transport problem can be defined as one-dimensional. A complete description of the code as well as some applications is available (Chapters 1 and 2 of the senior author's dissertation).

System Requirements

The following system is required:

An IBM or compatible Personal Computer with:

- 510 K or more available random access memory (RAM)
- EGA or VGA card and color monitor
- Math Coprocessor (optional but greatly enhances operational speeds)
- IBM or MS DOS 2.0 or above

A hard disk is highly recommended. Using a hard disk may significantly reduce the time for disk file reading/writing processes, which the program relies upon for data storage and retrieval.

Data Preparation

All input/output data are handled within the model environment; no other preprocessors are necessary. The input data are saved as a random access file on a disk, which can be retrieved and modified for later application. Output data are saved as an ASCII disk file, which can be routed to the printer or retrieved by spread sheet programs like Lotus 123 or Microsoft Excel. The output data are also displayed as breakthrough and profile curves on the screen during simulation.

No special requirements are necessary to initialize the program. Two demonstration data files must be included in the same directory of the executable file.

Error Handling

The program can identify a number of errors without terminating the simulation. Usually, when an error occurs, the program will display the error message and return to the beginning of the program. However, when improper graphic hardware is encountered, the program will display an error message and return to the operating system.

2. STEP BY STEP OPERATION GUIDE

Manual Format

This manual assumes that the user has some knowledge of basic DOS commands and is presented in a screen by screen format. Each screen guide consists of four components:

1. Display of the screen.

2. The screens from which the current screen originates.
3. Subsequent screen.
4. Description of the current screen.

Successive screens may not appear sequentially according to their number. Rather, the sequence depends upon the model structured by the user. The relationship among screens is presented in Figure 1.

To start the program, in the directory containing the executable file and at the DOS prompt, type MMGTM and press ENTER.

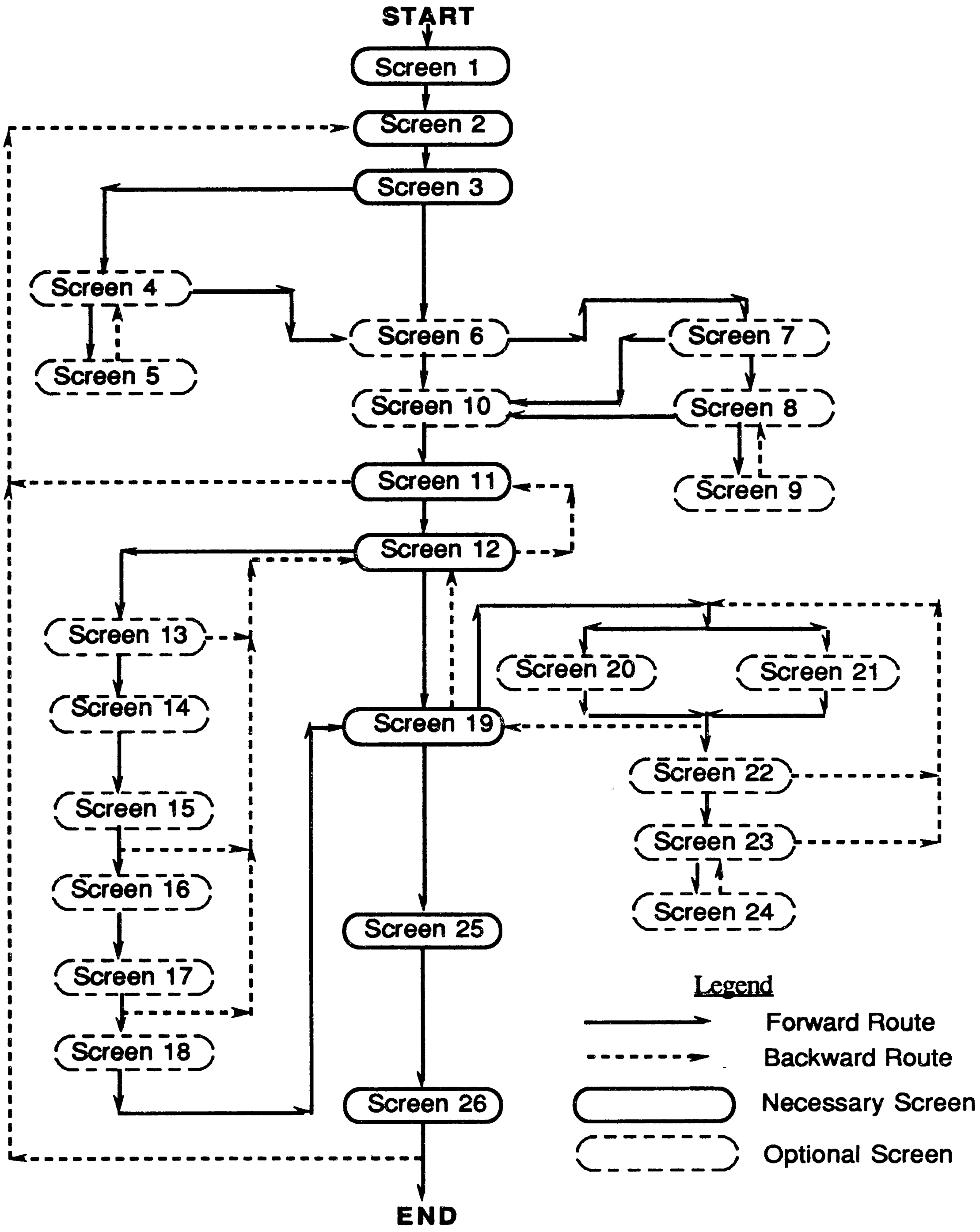
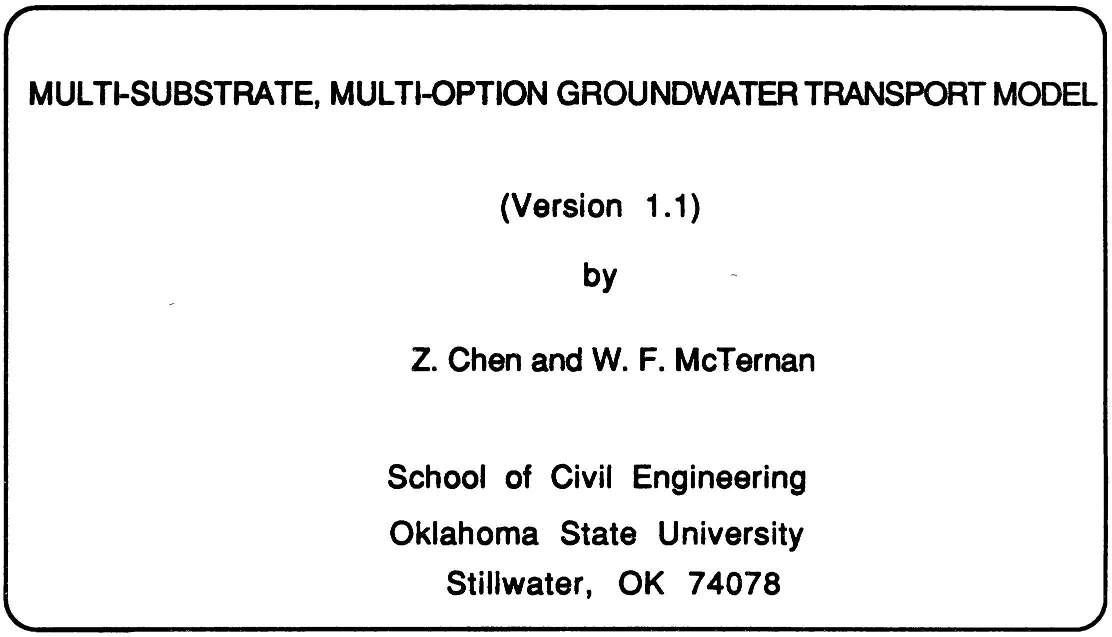


Figure 1. Screen Flowchart

Screen Description

SCREEN 1



MULTI-SUBSTRATE, MULTI-OPTION GROUNDWATER TRANSPORT MODEL

(Version 1.1)

by

Z. Chen and W. F. McTernan

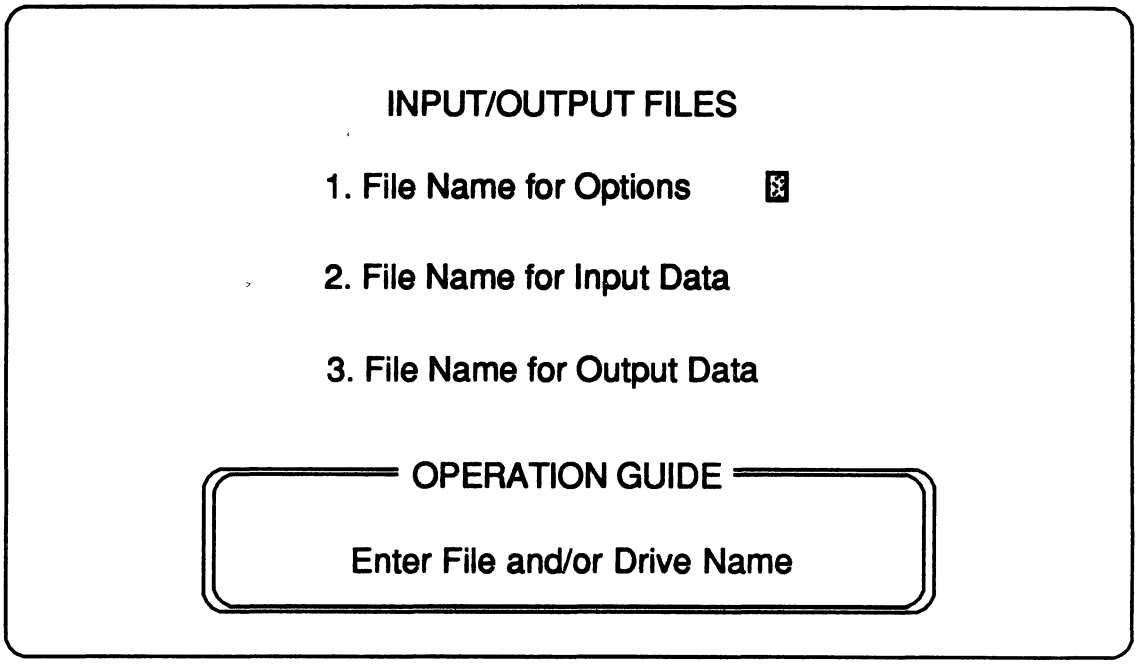
School of Civil Engineering
Oklahoma State University
Stillwater, OK 74078

From: Operating system.

To: Screen 2 (any key)

Description: This screen displays the program name, version number, authors and institution. If the program displays an error message instead of the above information, either the graphic display is incompatible, or there is not enough RAM to run the program. In this case, you have to use another computer or release some RAM, if possible. If no problems exist, screen 2 will appear if any key is hit.

SCREEN 2



INPUT/OUTPUT FILES

1. File Name for Options
2. File Name for Input Data
3. File Name for Output Data

OPERATION GUIDE

Enter File and/or Drive Name

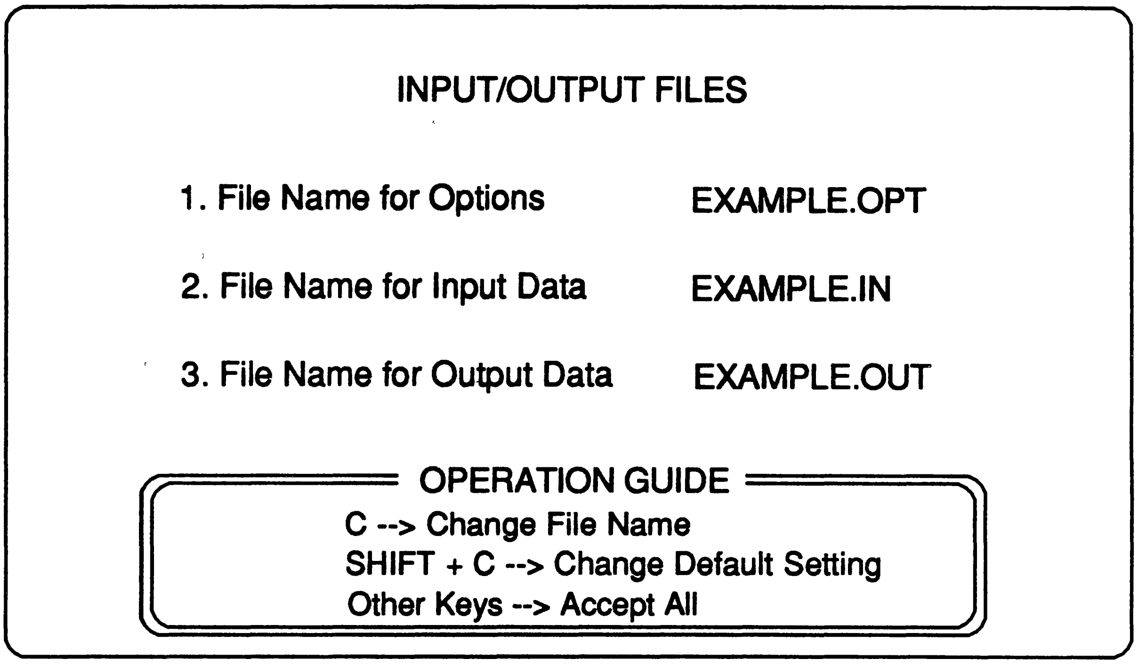
From: Screen 1; Screen 11, Screen 26.

To: Screen 3 (After entering the output file name)

Description: The program asks for input/output files. The file for options holds information on simulation options which you select in the simulation menu. The file for input contains all input parameters The file for output will hold the program output upon completion of the simulation. You can enter any valid file name, path, and drive according to DOS rules. If you enter the option and input file names which have been used previously and they are in the drive and path you specified, the model will load the data. Otherwise the file names are considered new, and you have to select simulation options and enter necessary input data from scratch before starting the simulation. The name you select for your output data will override any existing file with the same name.

It is suggested that you use the same name but a different extension for one simulation, for example, use "opt" extension for option file, "in" for input file and "out" for output file. Using this method can provide an easy identification for each simulation after you have run the program many times and created many files. If you use the suggested name extensions, after entering the option name and extension, you don't have to type the input and output file names. Just hit ENTER, and the same name with extension "in" and "out" will appear. If you don't enter any name, hitting ENTER will call the default data "demo.opt" and "demo.in". Make sure the default data files are in the same directory as the executable file if you use these default data.

SCREEN 3



INPUT/OUTPUT FILES

1. File Name for Options EXAMPLE.OPT
2. File Name for Input Data EXAMPLE.IN
3. File Name for Output Data EXAMPLE.OUT

OPERATION GUIDE

C --> Change File Name
SHIFT + C --> Change Default Setting
Other Keys --> Accept All

From: Screen 2.

To: Screen 4 (C); Screen 7 (SHIFT + C); Screen 11 (other key). Note: screens 6 and 10 may appear before screen 11, see descriptions in screens 6 and 10.

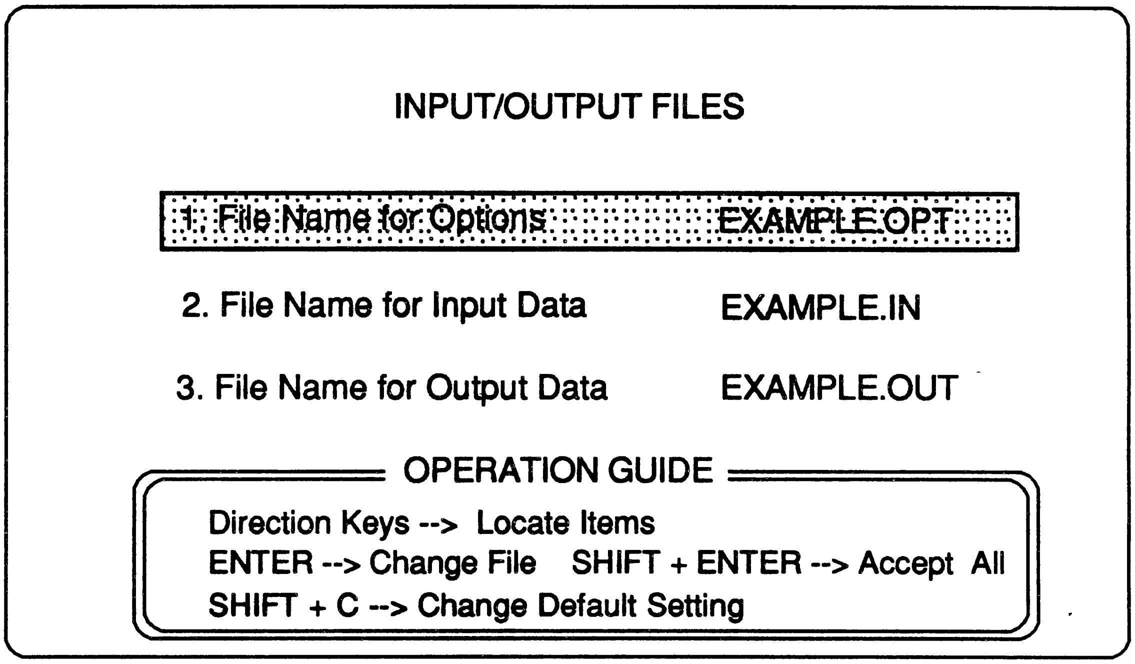
Description:

1. Change file name -- If you have entered a wrong file name or you want to change any file names you just entered, you may use this option.

2. Change default setting -- The default setting includes the maximum convergence error, the maximum iteration steps and file override option. If you want to change any of this, accept this option. Accepting this option also implies you accept the input/output file names you just entered. The default setting is used to control the internal running mode and is different from the default input data.

3. Accept All -- If the file names you entered are correct and you don't want to change the default setting, accept this option. The file names shown in screen 3 are for demonstration purposes. You should enter the appropriate names for your own simulation.

SCREEN 4



INPUT/OUTPUT FILES

1. File Name for Options EXAMPLE.OPT
2. File Name for Input Data EXAMPLE.IN
3. File Name for Output Data EXAMPLE.OUT

OPERATION GUIDE

Direction Keys --> Locate Items
ENTER --> Change File SHIFT + ENTER --> Accept All
SHIFT + C --> Change Default Setting

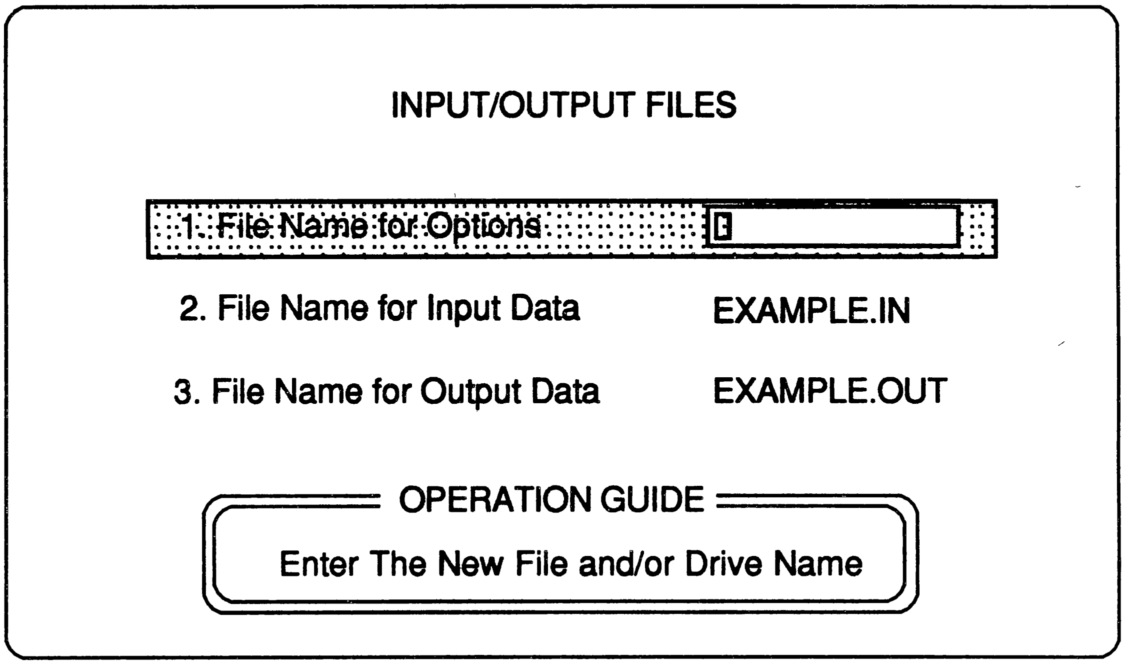
From: Screen 3, Screen 5.

To: Screen 5 (ENTER); Screen 11 (SHIFT + ENTER); Screen 7 (SHIFT + C).

Description:

- *Locate Items* -- Move the highlight to the item you want to change
- *Change File* -- Change the file name in the highlighted bar
- *Accept All* -- Accept all file names, without changing default setting
- *Change Default Setting* -- Accept the file names but want to change default setting.

SCREEN 5



INPUT/OUTPUT FILES

1. File Name for Options
2. File Name for Input Data EXAMPLE.IN
3. File Name for Output Data EXAMPLE.OUT

OPERATION GUIDE

Enter The New File and/or Drive Name

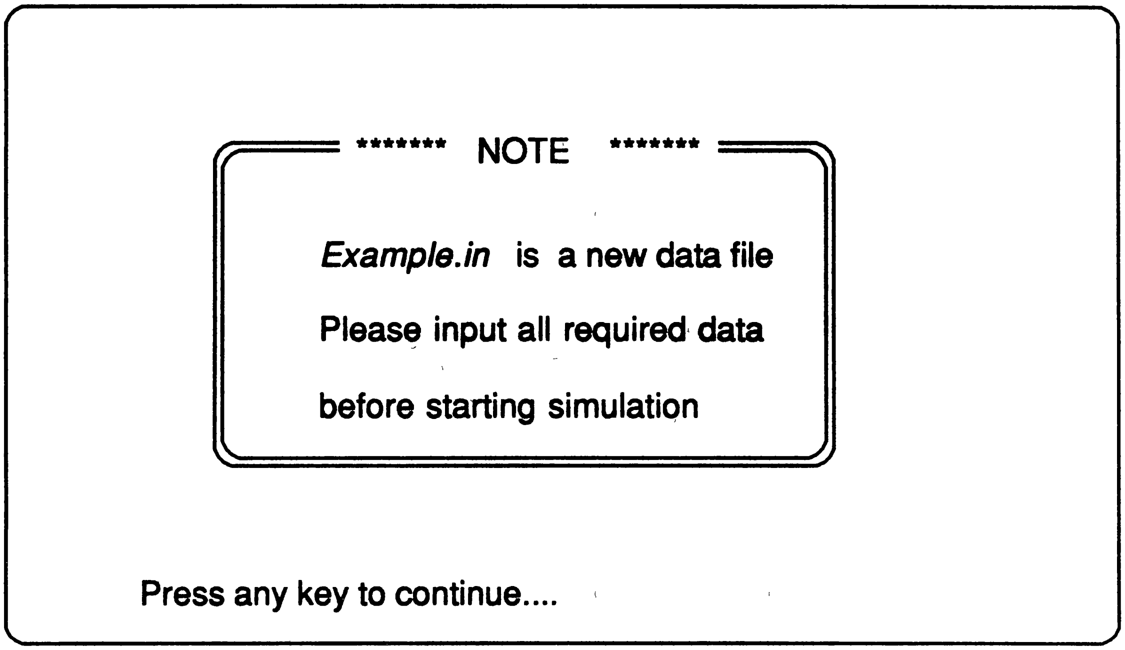
From: Screen 4

To: Screen 4 (after enter the new file name)

Description:

Type the new file name and press ENTER. The new name will appear and the highlight will move to the next item. Except for this, the new screen is the same as screen 4 and all key functions also remains the same.

SCREEN 6



******* NOTE *******

Example.in is a new data file

Please input all required data

before starting simulation

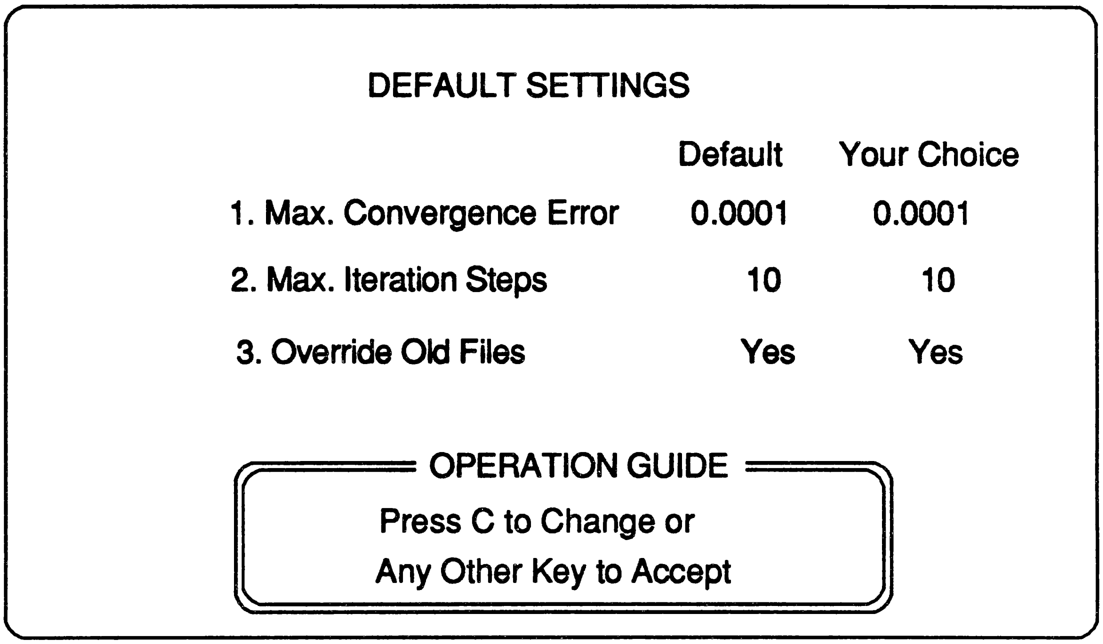
Press any key to continue....

From: Screen 4; Screen 3

To: Screen 7 (any key); Screen 11 (any key). The following screen depends upon the key strokes you applied in Screen 3 or Screen 4.

Description: This screen appears only when the input file name you entered before is new. It reminds you that the data file is new and empty. You must enter input data before starting simulation if this screen appears.

SCREEN 7



DEFAULT SETTINGS

	Default	Your Choice
1. Max. Convergence Error	0.0001	0.0001
2. Max. Iteration Steps	10	10
3. Override Old Files	Yes	Yes

OPERATION GUIDE

Press C to Change or
Any Other Key to Accept

From: Screen 3, Screen 4

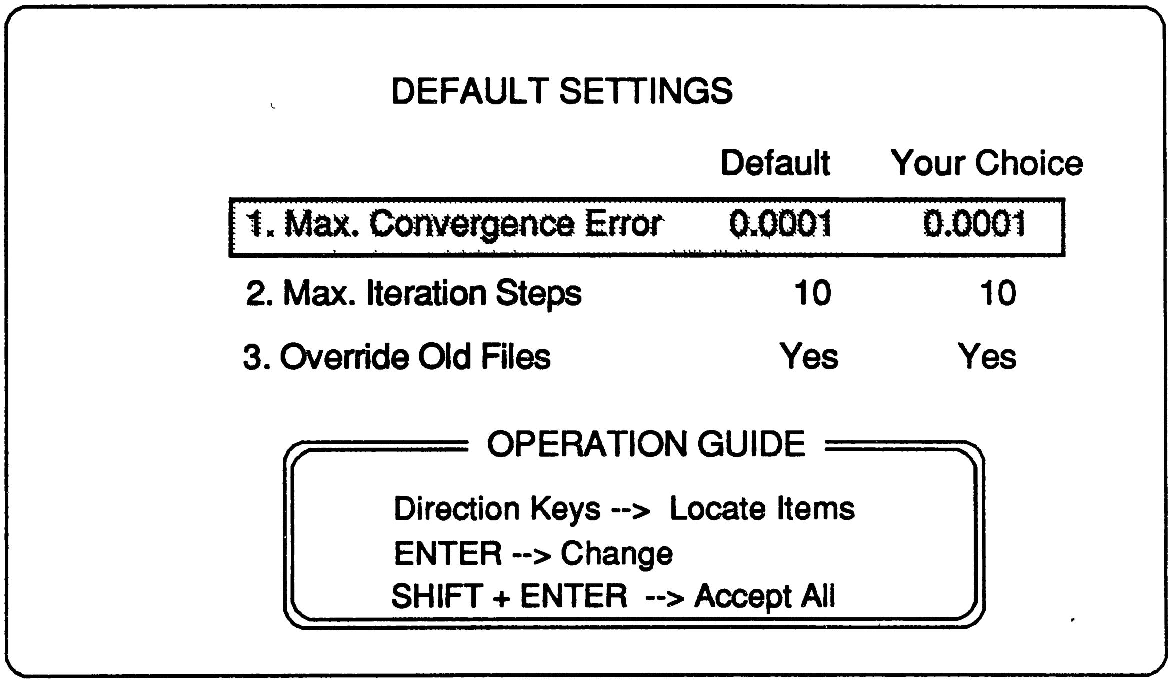
To: Screen 8 (C); Screen 11 (other keys)

Description:

- *Maximum Convergence Error* -- the program uses the Newton-Raphson method to solve non-linear algebraic equations resulting from some of the transport formulations that may be selected. After each iteration, the program checks for the maximum error from the trial solution. If the error is less than the value in the default setting, the trial solution is considered acceptable and the program moves to the next time step. The value of this setting should be appropriate to the magnitude of the contaminant concentration being simulated. Too small a value may result in prolonged simulation time or even simulation failure, while a large error setting may diminish the accuracy of the results.

- *Maximum Iteration Steps* -- Specifies the maximum number of iteration steps in each time step. If the error is still greater than the setting value after the specified number of iterations, the program will automatically halve the time increment, trying to minimize the error. If the error is still greater than the setting value and the maximum number of steps has been exceeded, the program will be terminated.
- *Override Old files* -- Choosing "Yes" causes the program to save any change you may make later to the old files, i.e. the old data files will be updated after each run. Selecting "No" directs the program to save any change you may make later to other files so that the data in the old files remain intact. If you choose "No", the program will ask you to enter new file names to hold the new data.

SCREEN 8



DEFAULT SETTINGS

	Default	Your Choice
1. Max. Convergence Error	0.0001	0.0001
2. Max. Iteration Steps	10	10
3. Override Old Files	Yes	Yes

OPERATION GUIDE

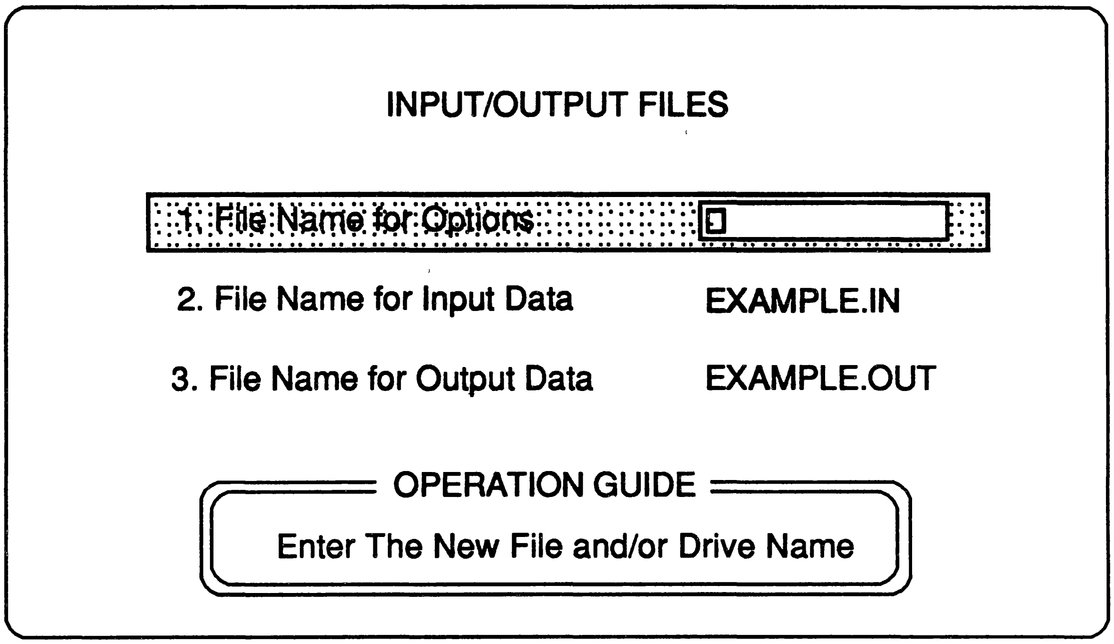
Direction Keys --> Locate Items
ENTER --> Change
SHIFT + ENTER --> Accept All

From: Screen 7

To: Screen 9 (ENTER); Screen 11 (SHIFT +ENTER)

Description: Similar to the operation for screen 4, you may move the highlight to an item you want to change by using the direction keys, and press ENTER to change the highlighted parameter.

SCREEN 9



INPUT/OUTPUT FILES

1. File Name for Options ☐

2. File Name for Input Data EXAMPLE.IN

3. File Name for Output Data EXAMPLE.OUT

OPERATION GUIDE

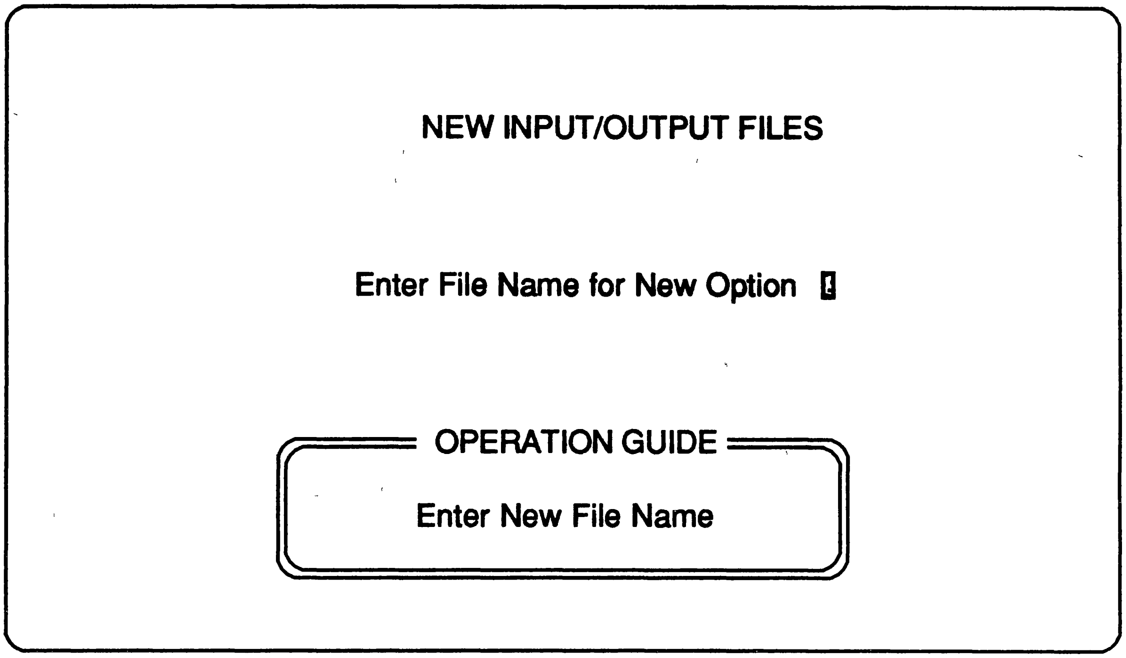
Enter The New File and/or Drive Name

From: Screen 8

To: Screen 8 (after entering the new value)

Description: Enter the value of your choice and press ENTER. The new value will appear and the highlight will move to the next item. After that, except for the new value and the highlight position, the screen is the same as Screen 8. The key functions also remain the same.

SCREEN 10



NEW INPUT/OUTPUT FILES

Enter File Name for New Option ▮

OPERATION GUIDE

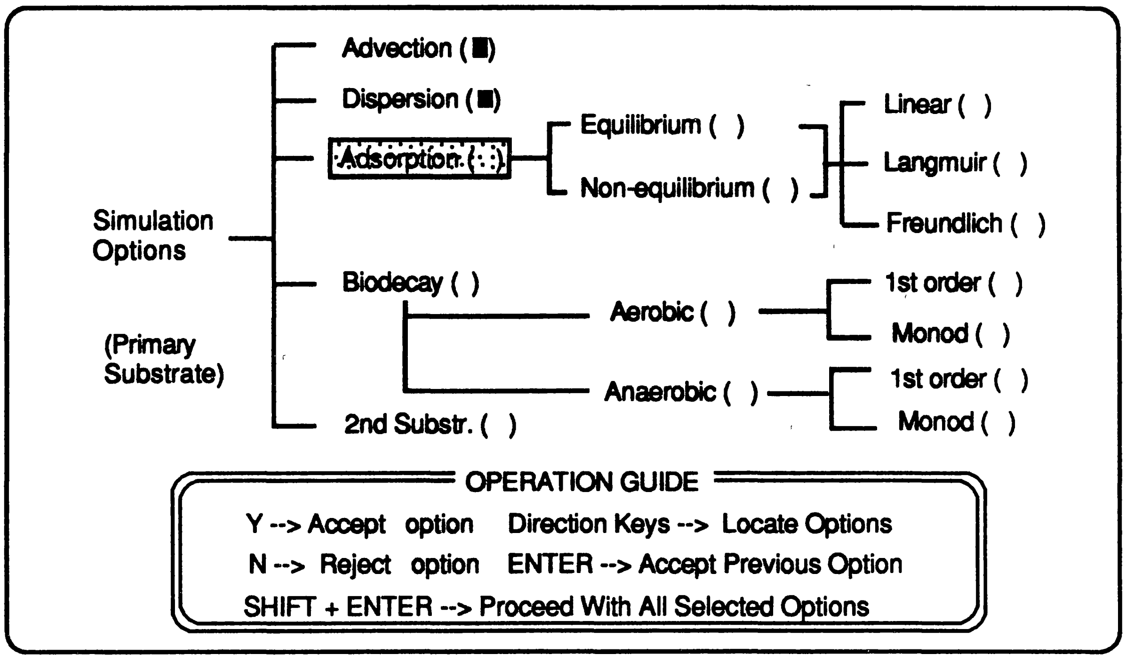
Enter New File Name

From: Screen 3, Screen 4, Screen 6, Screen 7, Screen 8

To: Screen 11 (after entering all names)

Description: This screen only appears when the "No" option to override the old file in the default setting is selected. The file names you enter under this screen will retain all changes you may make later. The data in the files you entered previously will remain unchanged. If you enter the same name as the old files, or press ENTER without a name, the program will automatically produce a name "NEW" with appropriate extension to avoid overriding the old data file. If you make no changes later, the program will copy the data in the old files to the files you entered under this screen.

SCREEN 11



OPERATION GUIDE

Y --> Accept option Direction Keys --> Locate Options

N --> Reject option ENTER --> Accept Previous Option

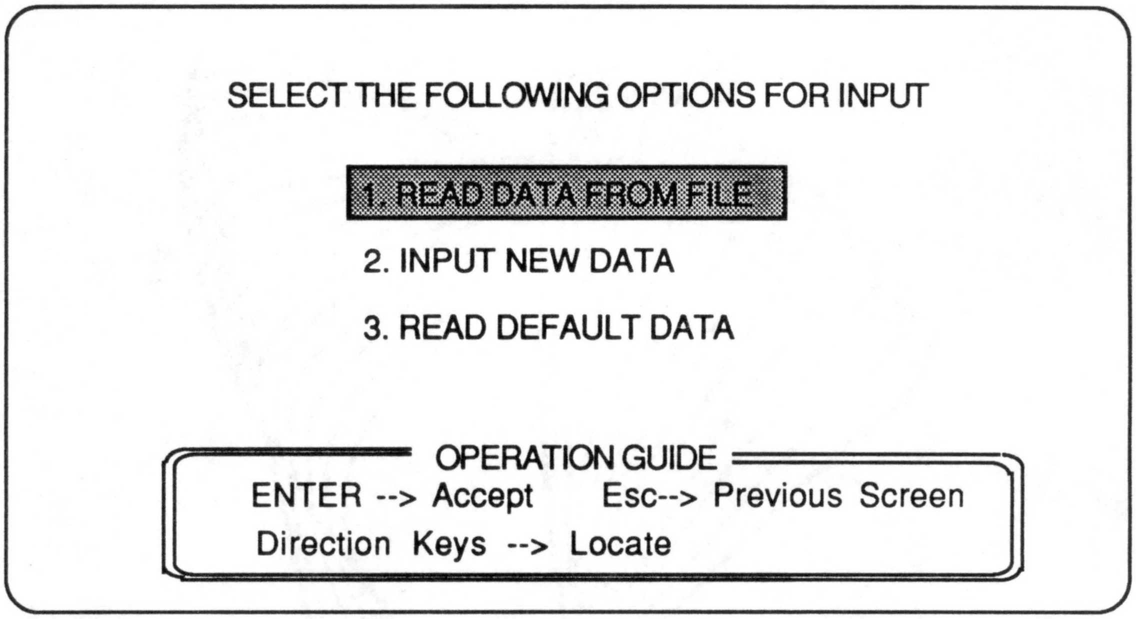
SHIFT + ENTER --> Proceed With All Selected Options

From: Screen 3, Screen 4, Screen 6, Screen 7, Screen 8, Screen 10

To: Screen 12 (SHIFT + ENTER); Screen 2 (Esc)

Description: A dot in the parenthesis indicates that the option is selected. If you use an option file which has been created previously, that option will appear on the screen. You can use the ENTER key and direction keys to move the highlight and select or delete the highlighted option by pressing "Y" or "N" key. After the selection, press SHIFT and ENTER simultaneously. If you have selected the option for secondary substrate, another option screen will appear to select appropriate simulation options. A beep sound and a message will appear when your selection is improper. If this happens, refer to the message and correct the selection.

SCREEN 12



From: Screen 11, Screen 13, Screen 15, Screen 17, Screen 19

To: Screen 19 (option 1, option 3); Screen 13 (option 2) Screen 11 (Esc).

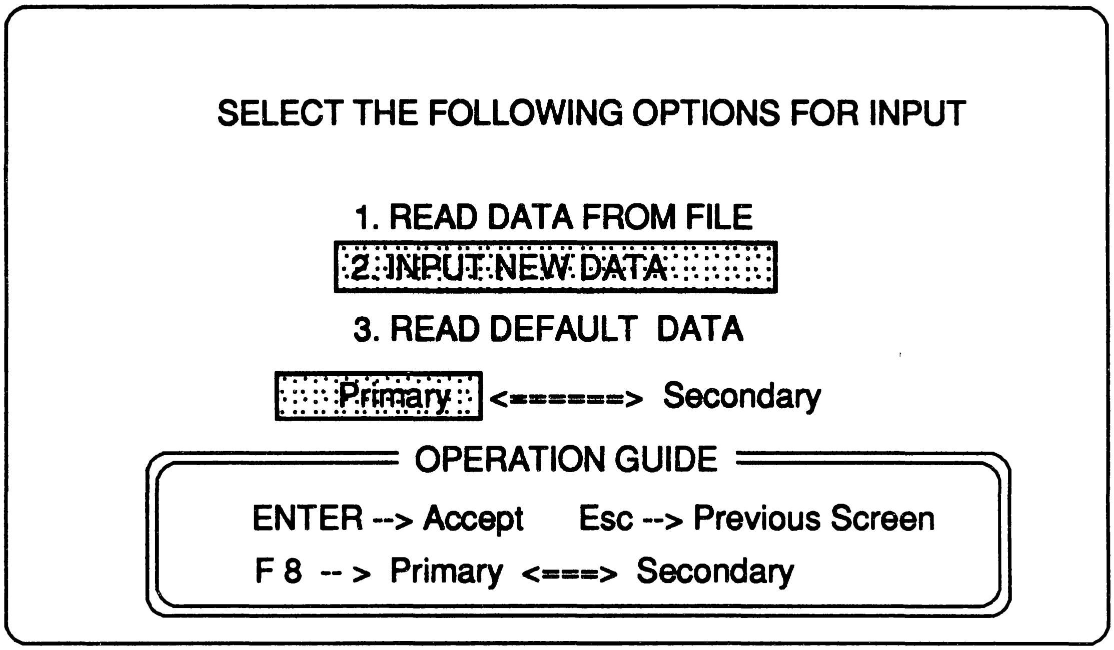
Description: You may move the highlight to the option you want by using the direction keys, then press ENTER to accept the highlighted option. You may also press the numerical key to select the corresponding option. If you use the numerical keys, the option corresponding to the number will be selected instantly regardless of the highlight position. The three options are discussed below:

1. Read data from file -- This option directs the program to read data from the disk file you entered under "File Name for Input Data". If the file has been previously created, the program will be ready for simulation after you accept this option. If the file is new, accepting this option will initialize all numerical data to zero and string data to null. Before you start the simulation, you must change all of the input data from zero to the value you want by using the "view or change parameters" option as described later in this manual. If the input file is new, it is suggested that you use the "Input New Data" option as described below.

2. *Input New Data* -- This option lets the program read input data from the key board. You may choose this option when you have created a data file the first time. If the input data file has been created previously, the input data you later enter from the key board will override these existing values.

3. *Read Default Data* -- This option is for demonstration use. This option causes the program to read the input data from the default data file, which is named "demo.in". This file was prepared for model demonstration and must be in the same directory containing the executable file. To use this option, you should have entered "demo.opt" and "demo.in" files at the beginning of the program. Otherwise a beep sound will be heard when you select this option and the program will not proceed. If you use this option you can later view the input data and start the simulation. Recall that these data cannot be changed by the user.

SCREEN 13



SELECT THE FOLLOWING OPTIONS FOR INPUT

1. READ DATA FROM FILE
2. INPUT NEW DATA
3. READ DEFAULT DATA

Primary <======> Secondary

OPERATION GUIDE

ENTER --> Accept Esc --> Previous Screen

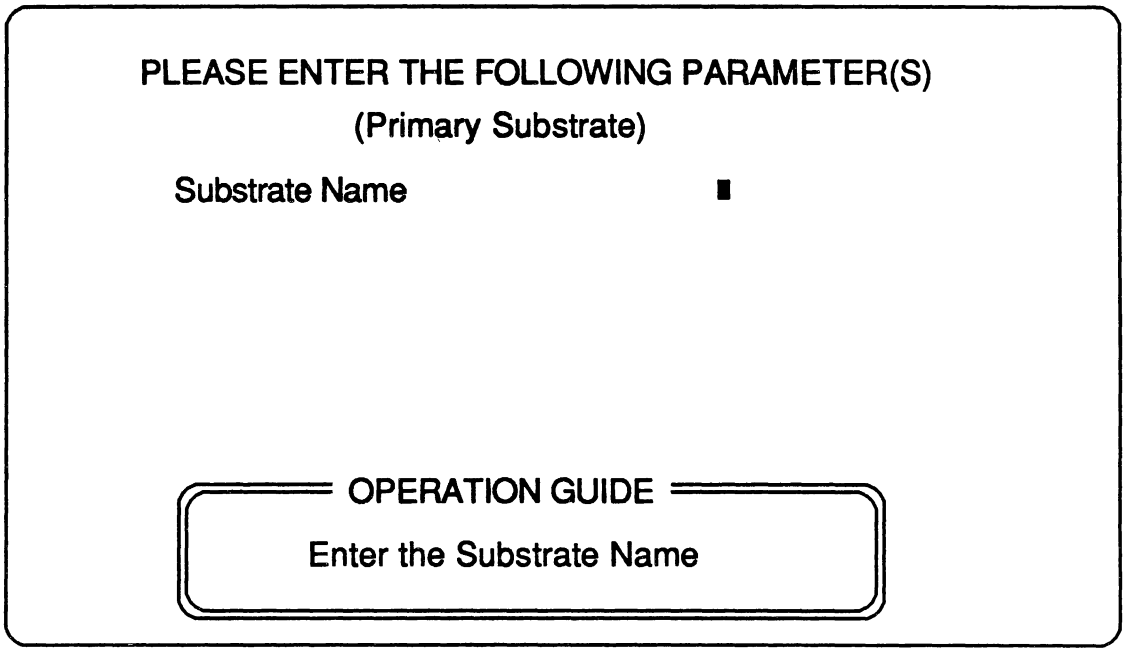
F 8 --> Primary <===> Secondary

From: Screen 12.

To: Screen 14 (ENTER); Screen 12 (Esc).

Description: By using the "F8" key, you may move the highlight to shuttle between "Primary" and "Secondary". If the input data file is empty, you may choose "Primary" and the program will prompt for input data on a line by line basis. If the file has previous data for a primary substrate, you may add a secondary substrate under screen 11 by selecting the "Secondary" option. In this case, the program will prompt for the input data for the secondary substrate while the previous data are unchanged. If you do not want to input any data, press Esc and Screen 12 will reappear. Key F8 only functions when simulation for secondary substrate has been selected.

SCREEN 14



PLEASE ENTER THE FOLLOWING PARAMETER(S)
(Primary Substrate)

Substrate Name ▮

OPERATION GUIDE

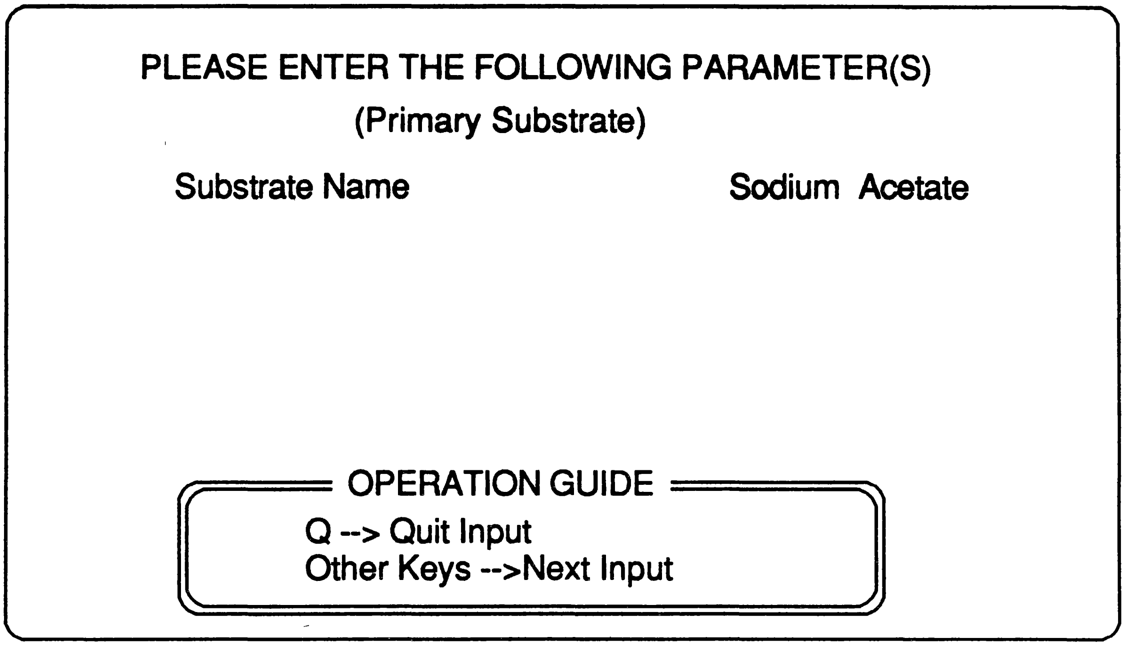
Enter the Substrate Name

From: Screen 13.

To: Screen 15 (After entering the substrate name).

Description: Enter the substrate name for primary substrate. This name is for reference purposes and does not have any effect on the simulation.

SCREEN 15



PLEASE ENTER THE FOLLOWING PARAMETER(S)
(Primary Substrate)

Substrate Name Sodium Acetate

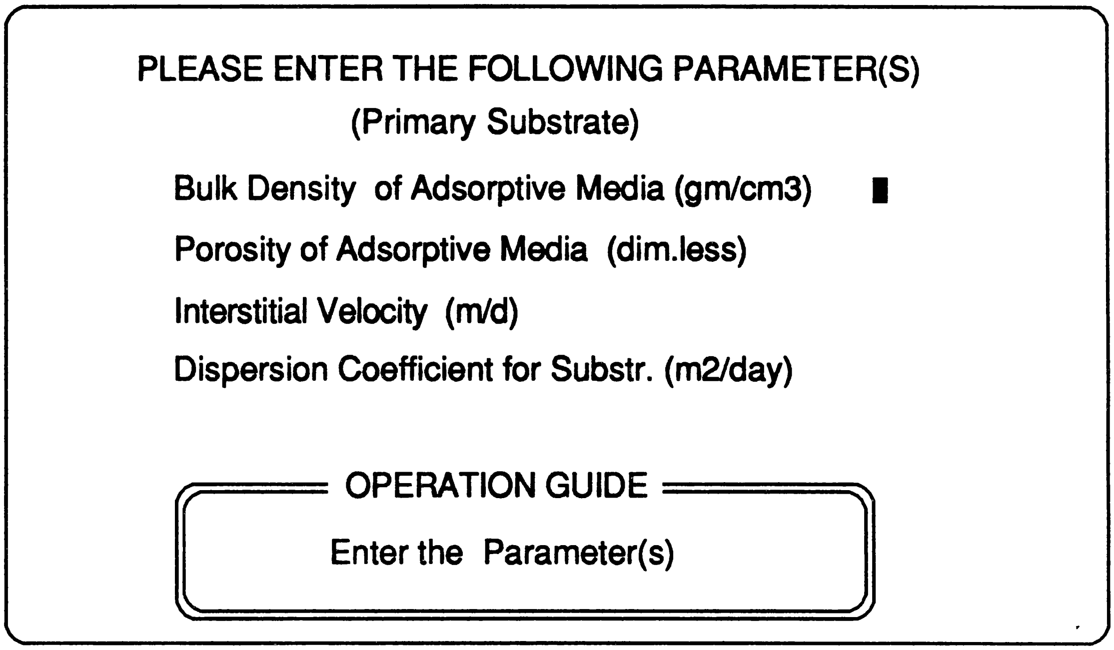
OPERATION GUIDE
Q --> Quit Input
Other Keys -->Next Input

From: Screen 13.

To: Screen 12 (Q); Screen 16 (other keys)

Description: This screen provides an option for you to quit the input process. If the data file is new, you may continue for next input. If you quit the input process, the data you have entered will be retained.

SCREEN 16



PLEASE ENTER THE FOLLOWING PARAMETER(S)
(Primary Substrate)

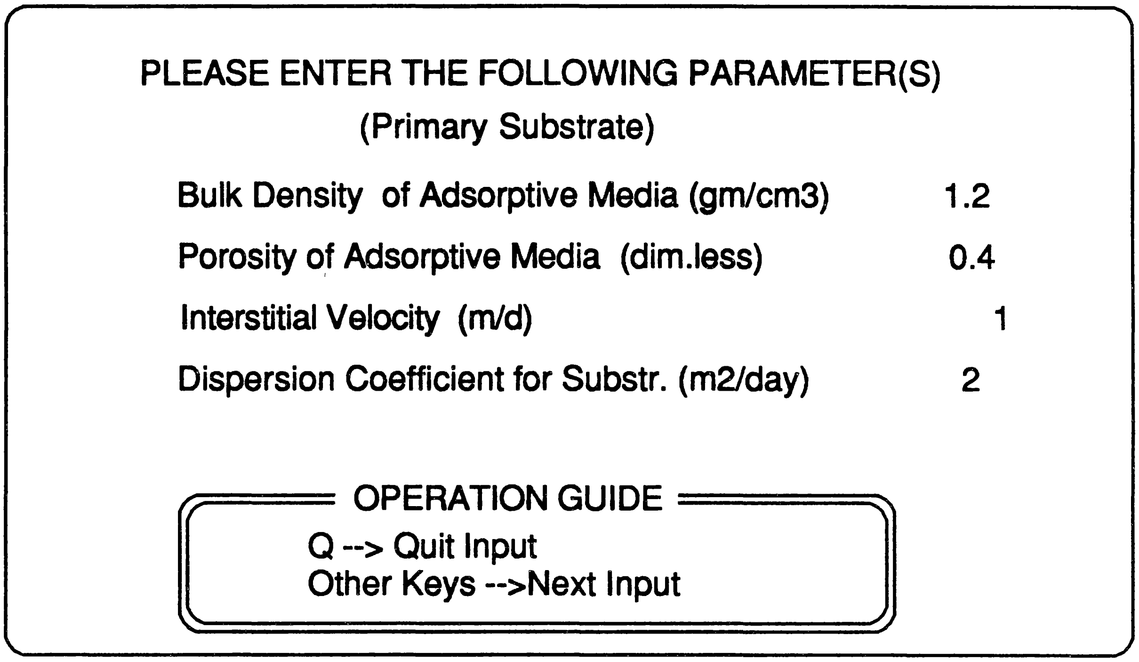
Bulk Density of Adsorptive Media (gm/cm3)
Porosity of Adsorptive Media (dim.less)
Interstitial Velocity (m/d)
Dispersion Coefficient for Substr. (m2/day)

From: Screen 15.

To: Screen 17(after entering all data).

Description: Enter the appropriate value for each parameter requested. You have to enter all parameters before going to the next screen. If you have entered wrong values, you will be able to correct them later.

SCREEN 17



PLEASE ENTER THE FOLLOWING PARAMETER(S)
(Primary Substrate)

Bulk Density of Adsorptive Media (gm/cm3)	1.2
Porosity of Adsorptive Media (dim.less)	0.4
Interstitial Velocity (m/d)	1
Dispersion Coefficient for Substr. (m2/day)	2

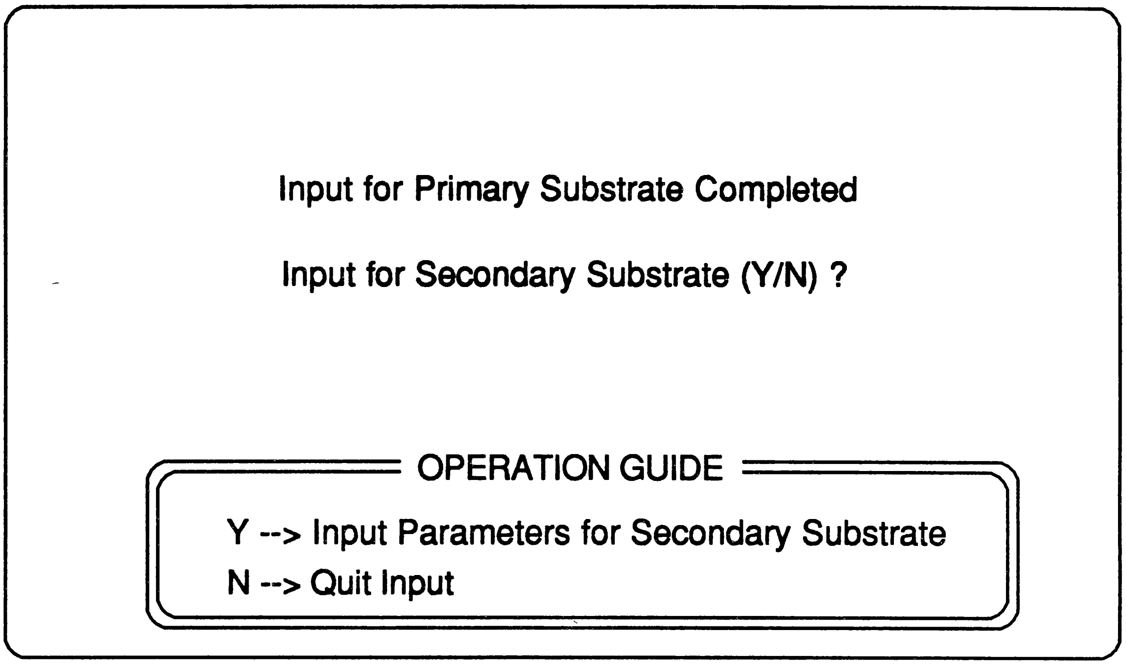
OPERATION GUIDE
Q --> Quit Input
Other Keys -->Next Input

From: Screen 16.

To: Screen 12 (Q); Screen 18(after entering all data for primary substrate).

Description: The values displayed in the screen are for demonstration purposes only, you should enter your own values for the simulation. For the function of "quit input" and "next input", please refer to the description under screen 15.

SCREEN 18



Input for Primary Substrate Completed

Input for Secondary Substrate (Y/N) ?

OPERATION GUIDE

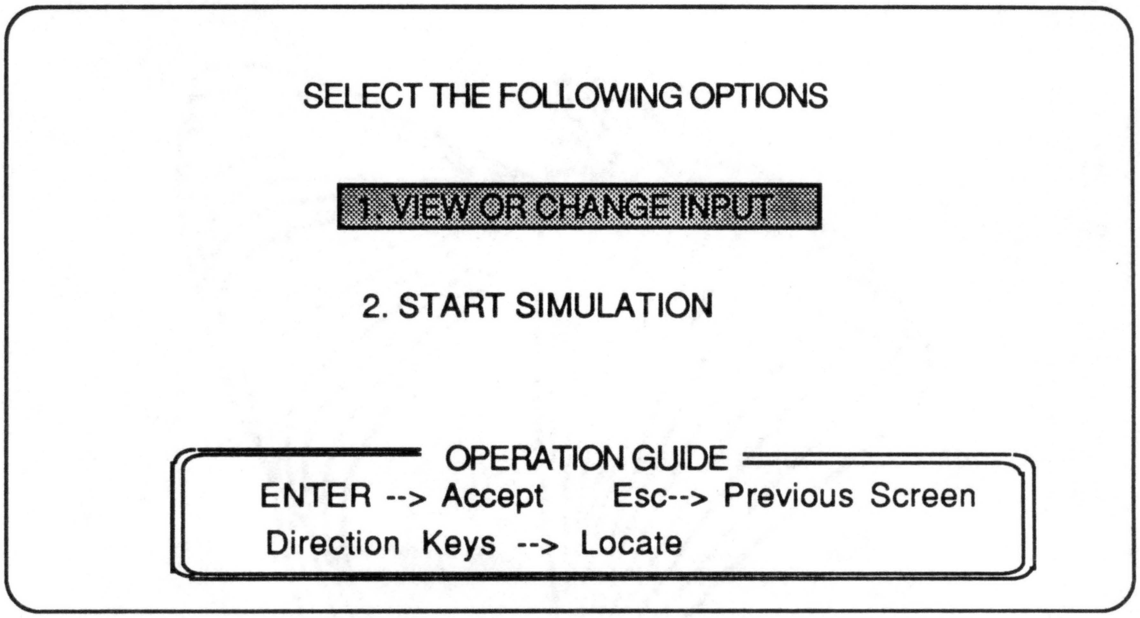
Y --> Input Parameters for Secondary Substrate
N --> Quit Input

From: Screen 17 (all of the primary substrate data have been input).

To: Screen 19 (N); Screen 14 (Y).

Description: This screen appears only when simulation for secondary substrate has been selected. This screen's appearance signifies that the data entry for primary substrate has been completed and a simulation detailing secondary substrate utilization is an option. Input the requested secondary substrate data if you have not done so previously. The process for data entry is the same as for primary substrate. Refer to Screens 14 through 17 for description.

SCREEN 19



SELECT THE FOLLOWING OPTIONS

1. VIEW OR CHANGE INPUT

2. START SIMULATION

OPERATION GUIDE

ENTER --> Accept Esc--> Previous Screen

Direction Keys --> Locate

From: Screen 12; Screen 18; Screen 20; Screen 21.

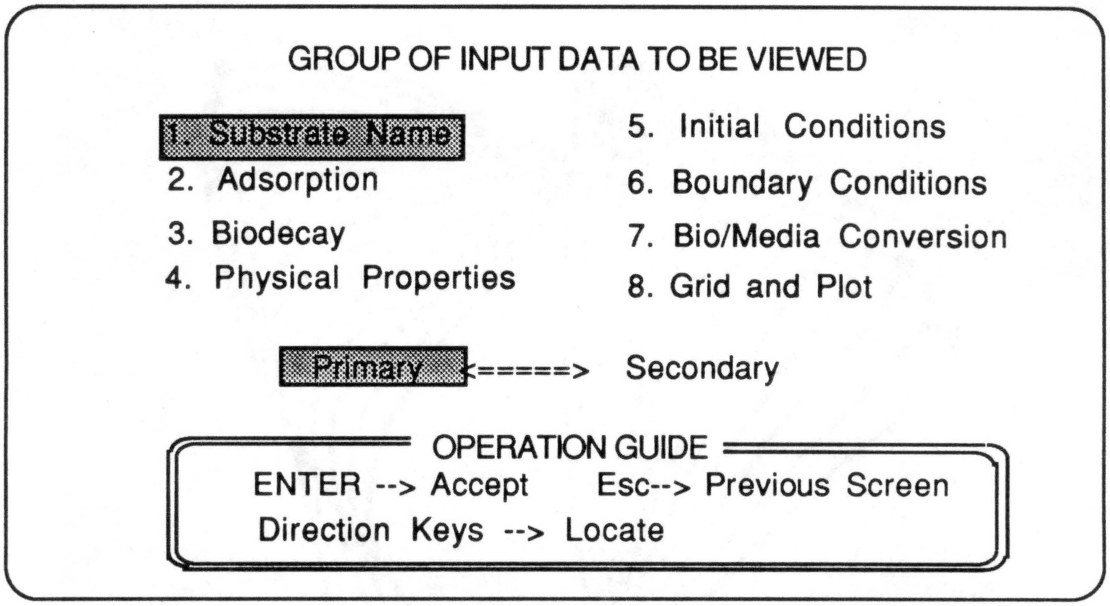
To: Screen 25 (option 2); Screen 20 or 21 (option 1); Screen 12 (Esc).

Description: You may move the highlight by using the direction keys and press ENTER to accept the highlighted option, or press the numerical key to accept the corresponding option instantly regardless of the highlight position.

1. View or Change Parameters -- You can use this option if you wish to review your input data, or if you wish to change them. If you are sure the input data are correct, choose option 2 instead.

2. Start Simulation -- This option starts the actual simulation with the updated input data. It is encouraged to check the input data before applying this option. Most simulation failures are caused by inappropriate or erroneous input data.

SCREEN 20

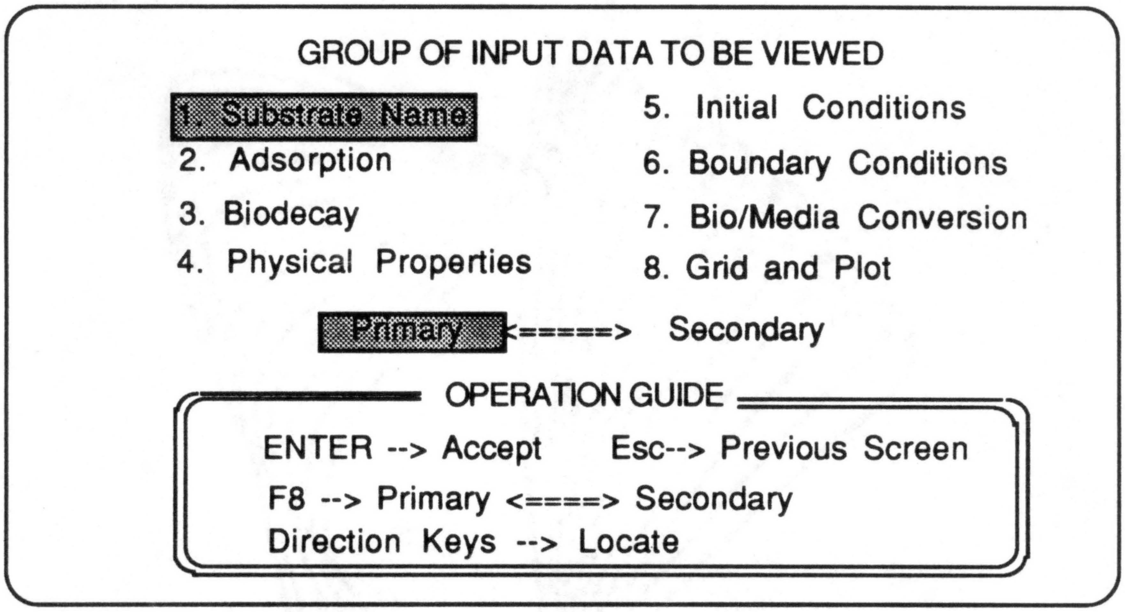


From: Screen 19; Screen 22; Screen 23.

To: Screen 22 (option 4); Screen 19 (Esc).

Description: This screen appears when the simulation for secondary substrate was not selected. The input data are grouped under eight titles of one or more parameters. If you wish to view a particular parameter value, move the highlight to the corresponding location and press ENTER. Pressing the proper numerical key selects the corresponding item instantly regardless of the highlight position. A beep will be heard if no data are available. This may happen, for example, when you want to see adsorption data but did not select the adsorption option in Screen 11. If you decide not to view any parameter and wish to begin simulation, press Esc to get Screen 19.

SCREEN 21



GROUP OF INPUT DATA TO BE VIEWED

1. Substrate Name
2. Adsorption
3. Biodecay
4. Physical Properties
5. Initial Conditions
6. Boundary Conditions
7. Bio/Media Conversion
8. Grid and Plot

Primary <=====> Secondary

OPERATION GUIDE

ENTER --> Accept Esc--> Previous Screen

F8 --> Primary <====> Secondary

Direction Keys --> Locate

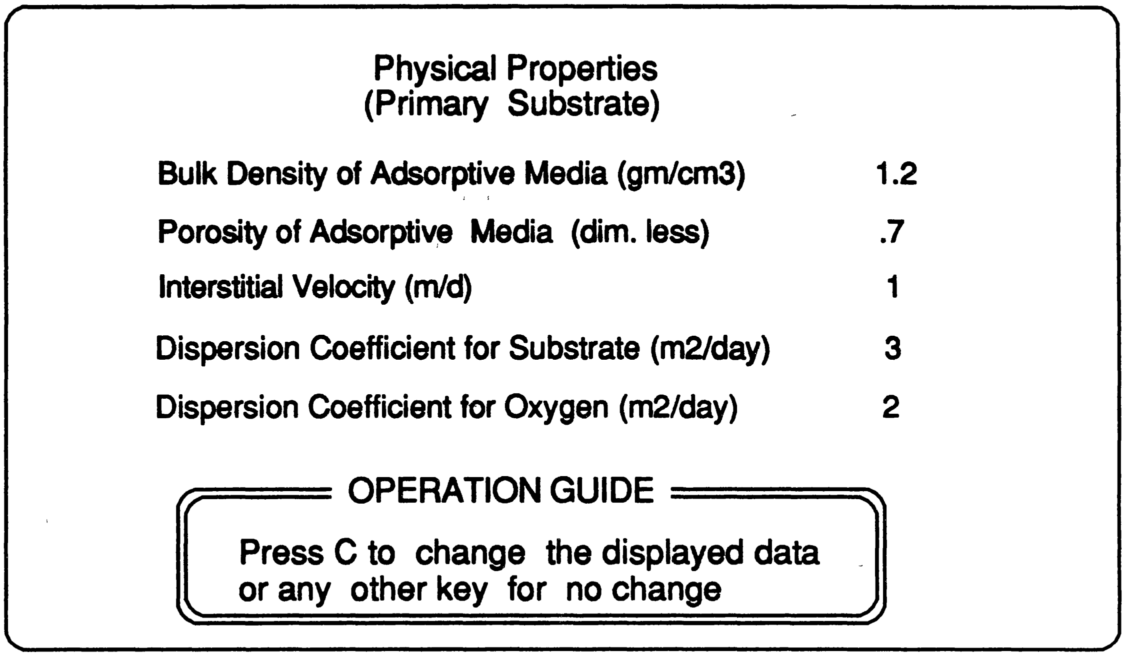
From: Screen 19; Screen 22, Screen 23.

To: Screen 22 (option 4); Screen 19 (Esc).

Description: This screen appears when simulation for secondary substrate was selected. This screen is basically the same as Screen 20 except that you can use key "F8" to shuttle the highlight between "Primary" and "Secondary" substrate options.

The data within group 8 (Grid and Plot) for secondary substrate are the same as previously stipulated for primary substrate. If you attempt to view the data under group 8 for secondary substrate, a beep sound will be heard and no data will be displayed.

SCREEN 22



Physical Properties
(Primary Substrate)

Bulk Density of Adsorptive Media (gm/cm3)	1.2
Porosity of Adsorptive Media (dim. less)	.7
Interstitial Velocity (m/d)	1
Dispersion Coefficient for Substrate (m2/day)	3
Dispersion Coefficient for Oxygen (m2/day)	2

OPERATION GUIDE

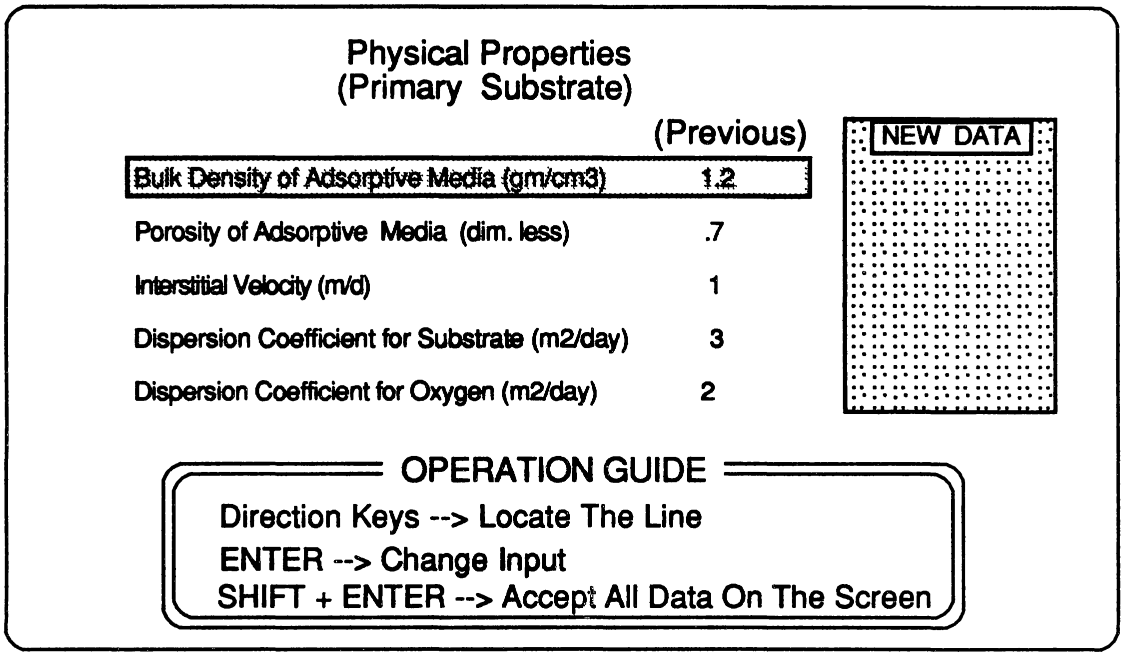
Press C to change the displayed data
or any other key for no change

From: Screen 20; Screen 21.

To: Screen 23 (C); Screen 20 or 21 (other keys).

Description: This screen displays the value of parameters in the group you selected on Screens 20 or 21. The physical property parameters are displayed here as an example. You may see different parameters and values, for primary or secondary substrate, depending upon the selections you made from Screens 20 or 21. If you wish to change any value of the displayed parameters, press C. Any other key will direct the program to accept this entire data set.

SCREEN 23



Physical Properties
(Primary Substrate)

	(Previous)
Bulk Density of Adsorptive Media (gm/cm3)	1.2
Porosity of Adsorptive Media (dim. less)	.7
Interstitial Velocity (m/d)	1
Dispersion Coefficient for Substrate (m2/day)	3
Dispersion Coefficient for Oxygen (m2/day)	2

OPERATION GUIDE

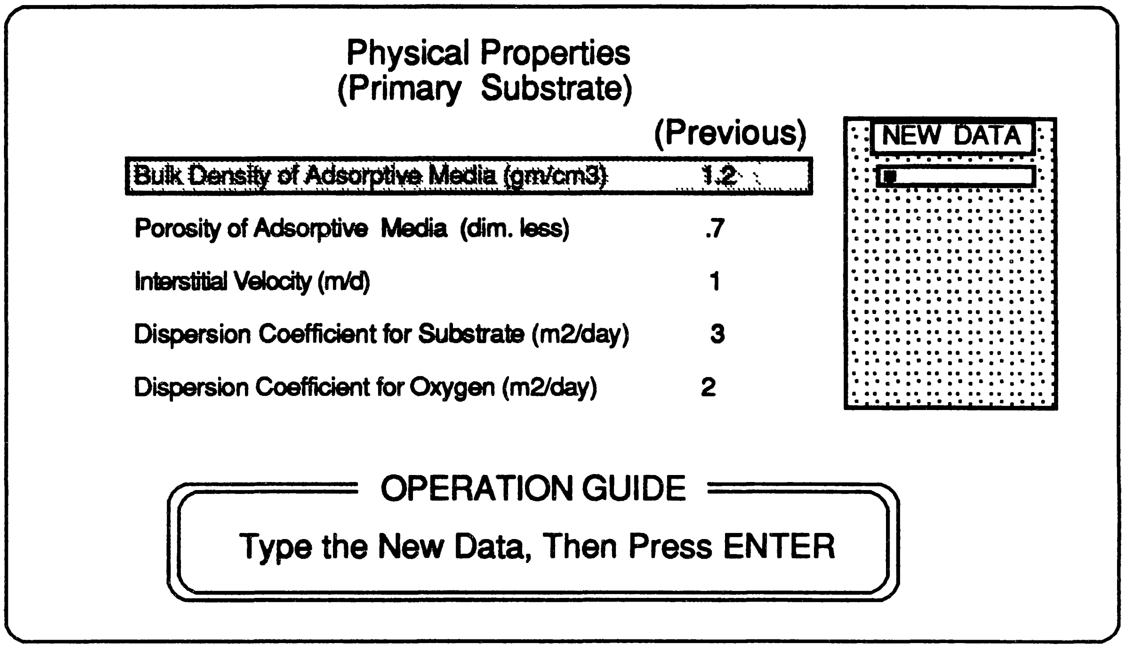
Direction Keys --> Locate The Line
ENTER --> Change Input
SHIFT + ENTER --> Accept All Data On The Screen

From: Screen 22.

To: Screen 24 (ENTER); Screen 20 or 21 (SHIFT + ENTER).

Description: After you move the highlight by using the direction keys to a particular item to change, press ENTER. If you accept the entire data set listed, press SHIFT + ENTER.

SCREEN 24



Physical Properties
(Primary Substrate)

	(Previous)
Bulk Density of Adsorptive Media (gm/cm3)	1.2
Porosity of Adsorptive Media (dim. less)	.7
Interstitial Velocity (m/d)	1
Dispersion Coefficient for Substrate (m2/day)	3
Dispersion Coefficient for Oxygen (m2/day)	2

OPERATION GUIDE

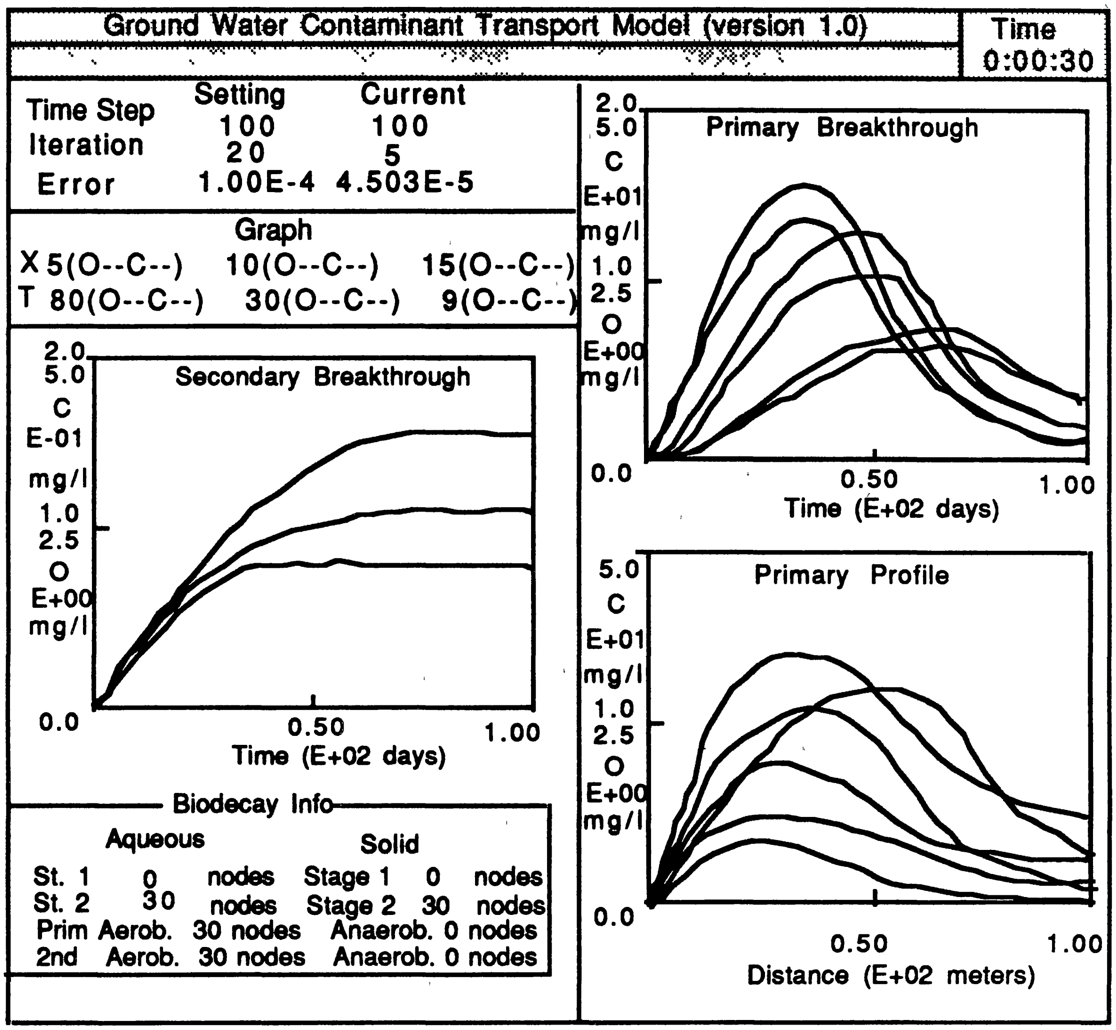
Type the New Data, Then Press ENTER

From: Screen 23.

To: Screen 23 (After entering a value of the parameter)

Description: Enter the new value of the highlight parameter. NOTE THAT YOU MUST ENTER A VALUE. You can not simply press ENTER to accept the previous value. After entering,the new value will appear within the NEW DATA area and the highlight will move to the next item. Except for this, the screen remains the same as screen 23 and all key functions remain the same.

SCREEN 25



Ground Water Contaminant Transport Model (version 1.0)

Time 0:00:30

	Setting	Current
Time Step	100	100
Iteration	20	5
Error	1.00E-4	4.503E-5

Graph

X 5(O--C--) 10(O--C--) 15(O--C--)

T 80(O--C--) 30(O--C--) 9(O--C--)

Biodecay Info

Aqueous		Solid	
St. 1	0 nodes	Stage 1	0 nodes
St. 2	30 nodes	Stage 2	30 nodes
Prim Aerob.	30 nodes	Anaerob.	0 nodes
2nd Aerob.	30 nodes	Anaerob.	0 nodes

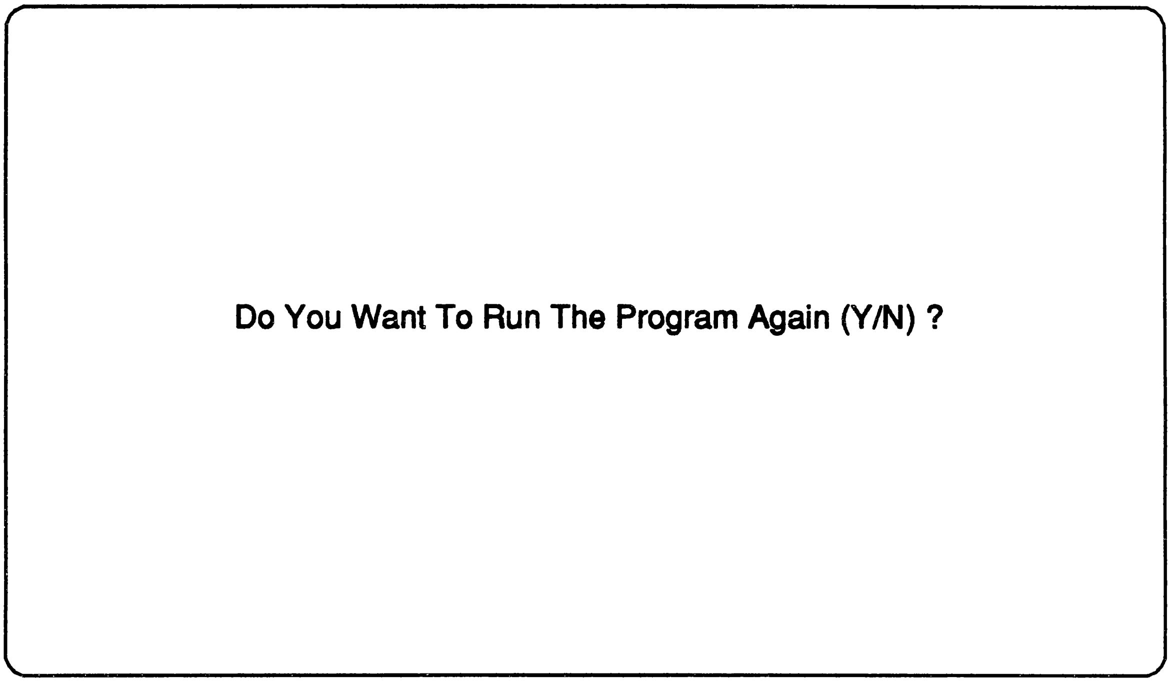
From: Screen 24.

To: Screen 26 (After completion of successful simulation)

Description: This screen appears after you start your simulation. The screen may look slightly different due to different simulation options. Three graphs are displayed: two breakthrough curves for primary and secondary substrates as well as oxygen, one profile curve for primary substrate and oxygen. The profile curve for the secondary substrate is not displayed due to space constraints but the data are saved in the output data file. The upper left corner of the screen shows the default simulation settings and the current simulation status. The upper right corner shows the time elapsed since the start of the simulation. The simulation time varies significantly, depending upon the options selected, the input data, as well as the computer hardware configuration. Upon completion, a beep sound will be heard and a message "Simulation completed" will blink.

There is software available to capture these screens to route to a printer. The authors feel, however, that the data files resulting from these simulations should be used for more precise work. These graphs, whether in hard copy or on the screen, are useful for comparisons.

SCREEN 26



Do You Want To Run The Program Again (Y/N) ?

From: Screen 25

To: Screen 2 (Y); Operating system (N)

Description: The simulation has been completed. If you want to run more simulations, press Y. In this case Screen 2 will reappear and you can run another simulation. If you want to quit the program, press N. The program will be terminated and the DOS prompt will appear.

2

VITA

Zhenquan Chen

Candidate for the Degree of

Doctor of Philosophy

Thesis: DEVELOPMENT AND APPLICATION OF A MULTI-SUBSTRATE, MULTI-OPTION GROUNDWATER TRANSPORT MODEL FOR UNCERTAINTY ANALYSIS

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