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Modeling contaminant partitioning between residual oil and mobile water phases in porous media: A time variant source of contamination

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MODELING CONTAMINANT PARTITIONING BETWEEN RESIDUAL OIL AND MOBILE WATER PHASES IN POROUS MEDIA - A TIME VARIANT SOURCE OF CONTAMINATION

by

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE MASTER OF SCIENCE

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Abstract

Modeling Contaminant Partitioning Between Residual Oil and Mobile Water Phases in Porous Media
-- A Time-Variant Source of Contamination

George C. Robinson

Residual hydrocarbons residing above or within an aquifer can serve as a continuous time-variant source of contamination to the aquifer. The primary mechanism for contamination is the movement of water past the immobile oil, leaching the partially soluble components from the oil phase into the aqueous phase, and transporting them to or within the aquifer. This research has focused on modeling the transport process. Three models for simulating the dissolution and transport from a residual oil zone are presented and evaluated: a "two-site" model, an "apparent" non-linear partitioning model, and a numerical equilibrium model. The two-site model is shown to be the most descriptive. The apparent partitioning model has been incorporated into a horizontal transport model. The capability and the limitations of the modified horizontal transport model are demonstrated for a hypothetical site. In addition, the effect of decoupling the transport equations for a multicomponent oil is investigated.
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Chapter 1

Introduction

Problem Description

Residual oil residing above or within an aquifer can serve as a continuous time-variant source of contamination to the aquifer. A common example of a residual source is the presence of gasoline which has leaked from an underground storage tank (LUST) into the surrounding soil and through natural and/or induced processes, remains at a residual saturation. Petroleum fuels are a common residual oil and are composed of various organic components which are slightly soluble in the aqueous phase. In general, the more soluble of these components, such as benzene, toluene, ethylbenzene, and xylene (BTEX), are of most concern based upon health risks associated with these components. The primary mechanism for contamination is the movement of water past the immobile oil, leaching the components from the oil phase into the aqueous phase, and transporting them to or within the aquifer. The time-variant character of the contaminant source is dependent upon several physical and chemical processes and a multitude of properties associated with the fluids and media.

Several attempts have been made in the past to characterize a contaminant source with models which incorporate selected processes and a wide range of simplifying assumptions. The
processes and simplifying assumptions selected are dependent on a variety of factors including the type of contaminant, the assumed location of the contaminant source, and the mobility of the phases present. The research presented here has focused primarily on modeling a multicomponent petroleum fuel which resides above the water table and is at a residual saturation. A schematic diagram of a residual oil source of contamination is shown in figure 1.1.

![Schematic diagram of a residual oil source of contamination.](image)

Figure 1.1  Schematic diagram of a residual oil source of contamination.

Although the focus of this research has been on modeling vertical infiltration past a residual oil source, much of the work can be extended to modeling a residual oil source which resides below the water table.
Research Objectives

The primary objectives of this research can be stated as follows:

1. Locate and evaluate contaminant transport models which might be applicable to modeling the dissolution of a residual oil source due to vertical infiltration of water.
2. Incorporate an appropriate contaminant transport model for the dissolution of a residual oil source into the horizontal transport model BIOPULSE II.
3. Demonstrate the applicability and the limitations of the modified transport model.

A secondary objective was identified as a result of the evaluation of contaminant transport models for the dissolution of a residual oil source. The secondary objective can be stated as follows:

4. Investigate the effect of decoupling transport equations for a multicomponent oil.

The first objective of this research was to locate and evaluate contaminant transport models which might be applicable to modeling the dissolution of a residual oil source due to vertical infiltration of water. Three models will be evaluated in this work. The first model evaluated is a modified version of the analytical transport model for two-site adsorption presented by Parker, et al. (1984). The second model evaluated is the analytical transport model presented by Wise,
et al. (To Be Submitted 1991). The third model evaluated is a modified version of the numerical transport model for adsorption presented by Kool, et al. (1989). Each of the models will be evaluated against the soil column experimental data presented by Borden, et al. (1989).

Several other more sophisticated models have been presented in recent years for modeling transport in multi-phase systems. Three of these models will be discussed in the literature review. The first is a model presented by Abriola, et al. (1985) which is applicable to four phase systems (soil, water, oil, and air) and includes multi-phase flow. A similar model has been presented by Corapcioglu, et al. (1987). Another model has been presented by Borden, et al. (1989) for three phase systems (soil, water, and oil). Furthermore, the model presented by Borden assumes the oil phase is immobile. The Borden model is the only one which has been evaluated against experimental data. Neither of these models have been evaluated in this work because they would be inappropriate to be used as a submodel to a horizontal contaminant transport model. They would be inappropriate because they are computationally expensive and the expense is not commensurate with the availability or accuracy of the required model parameters.

The second objective of this research was to incorporate an appropriate contaminant transport model for the dissolution of a residual oil source into the horizontal transport model BIOPLUME II. BIOPLUME II is the two-dimensional horizontal contaminant
transport model developed at Rice University by Rifai, et al. (1987). The result would be a model capable of characterizing the continuous time-variant source due to vertical infiltration past a residual oil source and the subsequent horizontal transport of the contaminants; this capability is currently not known to be available. The model selected to link to BIOPLUME II was the model presented by Wise et al. This was not necessarily the most appropriate of the three models evaluated, but was chosen due to the availability of the model at the time the link to BIOPLUME II was made.

The third objective of this research was to demonstrate the applicability and the limitations of the new model. The result is a model applicable to modeling the transport and fate of a residual oil source as previously described. The primary limitations are the limitations inherent in determining the necessary input parameters, such as the average pore water velocity infiltrating past the residual oil. Additional limitations are imposed by the transport model incorporated into BIOPLUME II: The transport equations are decoupled for the individual components of a multicomponent oil, there is no provision for biodegradation of the solute within the residual oil zone, the vertical infiltration is limited to a constant flux condition, and the model must be calibrated to site specific soil column data or a more sophisticated model prior to use.

A secondary objective was identified as a result of the evaluation of the various contaminant transport models. This objective was to investigate the effect of decoupling the transport
equations for a multicomponent oil. Each of the models evaluated in this work are applicable to the transport of only one component. Several investigators have presented models which couple transport equations for each component of a multicomponent non-aqueous phase liquid. The equations are coupled in order to develop a more accurate description of the oil/water partitioning through time. Unfortunately coupled equations require a numerical modeling approach which can be computationally expensive, particularly when mass transfer limitations are considered. The investigation presented here was initiated in an attempt to determine if and when coupling of the transport equations becomes necessary for adequately describing the dissolution of a component from a multicomponent oil.
Chapter 2

Literature Review

Researchers have only recently begun to focus on the problems associated with contamination which results from a residual hydrocarbon source. The recent focus is primarily a result of remediation efforts which have failed to clean up contaminated sites in the time frame initially expected.

The fundamental phenomena which govern the dissolution and subsequent transport of hydrocarbon components from a residual oil source are mass transfer and solute transport processes. A review of the most significant literature related to these processes is presented here.

The Local Equilibrium Assumption

The effluent concentration history from a residual oil source will be a function of the rate of dissolution of the hydrocarbon components to the aqueous phase. Several models have been developed which describe multiphase and multicomponent flow and transport in ground water aquifers (Abriola, et al., 1985; Corapcioglu, et al., 1987; Baehr, 1987; Sleep, et al., 1989). These models use the assumption of local equilibrium to describe the partitioning between the hydrocarbon, vapor, and aqueous phases. This implies that the concentration in each phase can be determined by equilibrium partitioning relationships, at the same spatial location, given the
concentration of at least one phase is known (Abriola, et al., 1985). Here spatial location is defined on a macroscopic scale such that equilibrium would be reached at the field measurement scale. The appropriate use of this assumption has yet to be determined (Powers, et al., 1991).

There have been several researchers from many disciplines who have contributed to the fundamental understanding of the dissolution of residual hydrocarbons. Some of the first contributions were the works of Van der Waarden, et al. (1971), Fried, et al. (1979), and Phannkuch (1984).

One of the earliest significant works was that of Van der Waarden, et al. (1971). Van der Waarden had undertaken a study of the transport of mineral oil components from a residual oil to an infiltrating water. The study was based primarily on the results of column experiments. The columns were packed with non-adsorbing glass particles and loaded to a residual saturation of a multicomponent mineral oil. The objective of Van der Waarden's work was to investigate the validity of the local equilibrium assumption. He concluded that the assumption was valid since equilibrium concentrations of the oil phase components were reached in the water phase. More recently, the conclusions reached by Van der Waarden have come into question.

Fried, et al. (1979) has presented a similar investigation to that of Van der Waarden. He also investigated the transfer of
hydrocarbons from a residual oil to an advecting water by means of column experiments. Separate experiments were conducted for columns loaded with a dual component oil and columns loaded with a multicomponent gas oil. Fried also conducted tests to evaluate the effect of pore water velocity. In these tests, the pore water velocities were varied from 2.5 m/d to 100 m/d. Fried concluded that equilibrium between the oil and water phases is reached within a few tens of cm for typical ground water pore velocities.

The primary significance of the works of Van der Waarden and Fried is that the local equilibrium assumption was widely accepted based on their conclusions. This subsequently resulted in an abundance of transport models based on the local equilibrium assumption. The validity of their conclusions however, has recently been questioned by many other researchers including Miller, et al. (1990) and Powers, et al. (1991). Miller pointed out that the experiments of Van der Waarden and Fried failed to investigate the change in non-aqueous phase liquid (NAPL) saturation as a function of time, included only a small range of NAPL saturation, and failed to quantify mass transfer coefficients. Miller concluded that overlooking these factors preclude any quantitative conclusions regarding the applicability of the local equilibrium assumption.

Phannkuch (1984) presented one of the first thorough works on mass transfer limitations applied to ground water contamination from a residual hydrocarbon. Phannkuch discussed conceptual models for the dissolution of a component from a residual oil into
water. He began by defining the principal steps for mass exchange as: 1) transport of the solute from the interior of the globule to the interface in multicomponent oils, 2) advective transport of water to the oil surface, 3) the dissolution reaction at the interface, and 4) the diffusive transport of dissolved products away from the interface in the water. He also pointed out that if the oil phase has a range of intermixed components of varying solubilities, selective leaching will take place where the more volatile components will dissolve first, leaving behind a less and less soluble residue.

Several field site case studies have been reported that show concentrations of organic solutes in groundwater lower than their equilibrium values (Mackay, et al., 1985). The rate limiting processes are suggested by Powers, et al. (1991) to include: (1) rate limited mass transport between phases, (2) physical by-passing of the aqueous phase around the contaminated region, (3) nonuniform flow of the aqueous phase due to aquifer heterogeneities, and (4) misinterpretation of the field data concentrations. Considerable research has focused on attempting to theoretically describe the rate limiting processes. These attempts tend to fall into two categories: chemical nonequilibrium models and physical nonequilibrium models.

**Two-Site/Two-Region Models**

The two-site/two-region models for transport of contaminants are mathematically similar models (Nkedi-Kizza, et al., 1984). These
models were developed in order to include both equilibrium and nonequilibrium processes in the solute transport equation. The two-region model is a physical nonequilibrium model and is obtained when apparent nonequilibrium processes are attributed to large heterogeneities in microscopic pore-water velocities (Parker, et al., 1984). This approach assumes that the liquid phase can be divided into two regions; a mobile region and an immobile region. This approach has been applied to modeling nonequilibrium adsorption processes by several researchers (Brusseau, et al., 1989; Rao, et al., 1980; Parker, et al., 1986; Gvitzman, et al., 1988; Cho, et al., 1990; Crittenden, et al., 1986; and Goltz, et al., 1986). Transport of a contaminant on a macroscopic scale is restricted to the mobile water region. Transfer into and out of the immobile liquid is assumed to be diffusion limited. Parker, et al. (1984) has presented the governing equations for the two-region model as follows,

\begin{equation}
(\theta_m + f\rho K) \frac{\partial c_m}{\partial t} + (\theta_{im} + (1-f)\rho K) \frac{\partial c_{im}}{\partial t} = \theta_m D_m \frac{\partial^2 c_m}{\partial x^2} - q \frac{\partial c_m}{\partial x} \tag{2.1}
\end{equation}

and

\begin{equation}
(\theta_{im} + (1-f)\rho K) \frac{\partial c_{im}}{\partial t} = \alpha^* (c_m - c_{im}) \tag{2.2}
\end{equation}

where \( c_m \) and \( c_{im} \) are the aqueous phase concentrations of the mobile and immobile aqueous regions, respectively (ML\(^{-3}\)), \( \theta_m \) and \( \theta_{im} \) are the mobile and immobile volumetric water contents, \( D_m \) is the dispersion coefficient for the mobile region (L\(^2\)T\(^{-1}\)), \( f \) is the fraction of the adsorption sites that equilibrate with the mobile aqueous phase, \( \alpha^* \) is a first order rate constant that governs the rate of solute
exchange between the two regions \((T^{-1})\), \(\rho\) is the bulk density of the porous media \((ML^{-3})\), \(K_d\) is the equilibrium partition constant \((L^3M^{-1})\), \(x\) is distance \((L)\), \(q\) is the pore water flux \((LT^{-1})\), and \(t\) is time \((T)\).

Several researchers have presented methods of independently determining the first order rate constant for the two-region model, including Rao, et al. (1980) and Brusseau, et al. (1989). These methods generally take either a physical diffusion model approach or use a first order mass transfer expression. In either case, a structured soil system is assumed in order to describe the geometry of the system.

The two-site nonequilibrium model is a more interesting model with respect to modeling dissolution from a residual hydrocarbon source. This model was developed as a chemical nonequilibrium model where the nonequilibrium process is assumed to be the result of a time-dependant reaction rate. This model has been used extensively for evaluating transport of adsorbing solutes (Cameron, et al., 1977; Lindstrom, 1976; Miller, et al., 1984; Selim, et al., 1988; Nkedi-Kizza, et al., 1984; and Lassey, 1988). This model assumes that adsorption occurs on two types of sites, one governed by equilibrium adsorption (type-1 site) and the other by first order kinetic non-equilibrium adsorption (type-2 site). Parker, et al. (1984) have developed a computer code for evaluating soil column breakthrough curves with the two-site model. The governing equations for the model, as presented by Parker, are as follows:
\[
(1 + \frac{f \rho K_d}{\theta_w}) \frac{\partial c}{\partial t} + \frac{\rho}{\theta_w} \frac{\partial s_2}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x}
\]  

(2.3)

and

\[
\frac{\partial s_2}{\partial t} = \alpha \left[(1-f)K_d c - s_2\right]
\]

(2.4)

where \( c \) is the aqueous phase concentration of the solute (ML\(^{-3}\)), \( s_2 \) is the type-2 site adsorbed concentration per unit mass of the solid phase (MM\(^{-1}\)), \( \rho \) is the bulk density of the porous media (ML\(^{-3}\)), \( f \) is the fraction of type-1 adsorption sites to all sites, \( K_d \) is the equilibrium partition constant (L\(^3\)M\(^{-1}\)), \( x \) is distance (L), \( t \) is time (T), \( D \) is a dispersion coefficient (L\(^2\)T\(^{-1}\)), \( v \) is the pore water velocity (LT\(^{-1}\)), \( \theta_w \) is the volumetric water content (L\(^3\)L\(^{-3}\)), and \( \alpha \) is a first order rate coefficient (T\(^{-1}\)).

The two-site nonequilibrium model is a more interesting model with respect to modeling dissolution because of the analogy which can be drawn between two-site adsorption and two-site dissolution. Borden, et al. (1989) were one of the first to present a model based on the two-site theory for the dissolution from a residual oil source. Most recently, Powers, et al. (1991) have presented a similar model based on the two-site theory for the dissolution from a residual oil source. The analogy and use of this model for dissolution and transport from a residual oil source is presented in greater detail in the third chapter of this work.
A First Order Kinetic Model

A first order linear resistance model is the mass transfer relationship used by the two-site model to describe the nonequilibrium process. Lapidus, et al. (1952) are generally credited with being the first to apply this type of relationship to investigate the dynamic behavior of an adsorption column. Generally, a first order linear resistance model implies that the net flux of a chemical species across an interface between two phases results from differences between the temporal and equilibrium concentrations of that species (Powers, et al., 1991). When applied to the dissolution of a hydrocarbon component from a residual oil, the net flux of the component is limited primarily by diffusion of the component through a boundary layer at the interface to the bulk aqueous phase (Phannkuch, 1984). The general form of this equation as presented by Powers, et al. (1991) is,

\[ F_i = -k_m (C_i - C_{si}) \]  

(2.5)

where \( F_i \) is the flux of the component \( i \) across the boundary layer per unit cross section area (\( MT^{-1}L^{-2} \)), \( -k_m \) is the mass transfer coefficient for component \( i \) across the boundary layer (\( LT^{-1} \)), \( C_i \) is the mass concentration of \( i \) in the bulk aqueous solution (\( ML^{-3} \)), and \( C_{si} \) is the aqueous phase equilibrium mass concentration of \( i \) (\( ML^{-3} \)).

A considerable amount of theoretical and experimental work has been performed in order to be able to predict the mass transfer
coefficient for given two phase systems (Miller, et al., 1990). Nernst
is credited with the first application to mass transfer in which the
solute is assumed to diffuse through a thin, stagnant boundary layer
of fluid surrounding a solid particle (Levich, 1962). This model has
subsequently been applied in numerous other studies of mass
transfer between a residual oil and an aqueous phase. The stagnant
film model defines the mass transfer coefficient by,

\[ k_m = \frac{D_1}{\delta} \quad (2.6) \]

where \( D_1 \) is the free liquid diffusivity of the solute and \( \delta \) is the
thickness of the stagnant film layer (Miller, et al., 1990). Miller
points out that the stagnant film model is deficient in two respects:
(1) liquid motion has been observed at distances much less than \( \delta \)
away from the solid surface, and (2) computed values of \( \delta \) have been
found to be a function of \( D_1 \). These deficiencies prevent an a priori
estimate of the thickness of the stagnant film layer. Miller also
points out that for many multiphase systems, mass transfer between
phases is the combined result of both advective and diffusive
processes, as well as other phenomena such as chemical kinetics and
density motivated flow. Miller concludes that determination of the
mass transfer coefficient would therefore require knowledge of the
velocity distribution at a small scale.

Both Miller, et al. (1990) and Powers, et al. (1991) discuss the
application of mass transfer correlations to the problem of
dissolution from a residual oil. Furthermore, the results of this type
of application has been presented by Phannkuch (1984). These empirical relationships are typically based on the Sherwood number which is a dimensionless parameter that relates interphase mass transport resistances to molecular mass transport resistances (Weltry, et al., 1969). However, Miller, et al. (1990), Powers, et al. (1991), and Phannkuch (1984) have all concluded that these correlations are not directly characteristic of the dissolution of a system of residual oil in porous media due to the type systems and assumptions they were designed for.

An alternative definition of the mass transfer coefficient which has been employed frequently was presented by Miller, et al. (1990) as,

\[ k_m = k_l \frac{A_{na}}{V} \]  \hspace{1cm} (2.7)

where \( A_{na} \) is the interfacial area between the residual oil and the aqueous phase \( (L^2) \), \( V \) is the volume of the porous medium \( (L^3) \), and \( k_l \) is a diffusion coefficient \( (L^2 T^{-1}) \). Miller points out that most experimental studies involve the measurement of \( k_m \) rather than \( k_l \), and so quantification of the specific interfacial area \( \frac{A_{na}}{V} \) is important. Unfortunately, as Miller and Phannkuch have both pointed out, the heterogeneous nature of the porous media structure make it difficult to quantify the actual internal contact area. In addition, there will exist not just one characteristic contact area, but a distribution of contact areas as there will be a continuum of blob
shapes and sizes (Mayer, et al., 1990). Furthermore, the interfacial area of the residual oil blobs will change continuously with time as the oil weathers.

**Recent Advancements**

Within the last three to five years there has been a considerable amount of literature published related to modeling the dissolution from a residual oil source. The recent works presented by Borden, et al. (1989), Rixey, et al. (1990), Miller, et al. (1990), and Powers, et al. (1991) were particularly relevant to the work presented in this thesis.

**Experimental Work and Two-Site Model Application by Borden et al.**

Borden, et al. (1989) were one of the first to present a model based on the "two-site" theory for the dissolution from a residual oil source. As previously discussed, the two-site theory has been used extensively in modeling adsorption phenomenon in soil column studies.

Borden's model was a one-dimensional finite difference transport model which simultaneously solved the transport equations for each component of a multicomponent oil. This "coupling" of transport equations was an effort to account for the time dependant partitioning of components which results from the selective leaching of components from a residual oil. The formulation
of the transport equations was analogous to that which had been based on the two-site theory for adsorption. The analogy is that there are two types of dissolution sites, one governed by instantaneous equilibrium dissolution and the other by mass transfer limited dissolution. The transport equations were presented as follows:

\[
\frac{\partial C_i^a}{\partial t} + \frac{\partial C_i^{of}}{\partial t} + \frac{\partial C_i^{os}}{\partial t} = \frac{\partial}{\partial z} \left[ D \frac{\partial C_i^a}{\partial z} \right] - \frac{\partial (v C_i^a)}{\partial z} \tag{2.8}
\]

\[
\frac{\partial C_i^{of}}{\partial t} = \left[ \frac{\sum C_i^{of} \gamma_i^a}{S_i \gamma_i^{of}} \right] \frac{\partial C_i^a}{\partial t} \tag{2.9}
\]

\[
\frac{\partial C_i^{os}}{\partial t} = K_m C_i^a - \frac{S_i \gamma_i^{os} C_i^{os}}{\sum C_i^{os} \gamma_i^a} \tag{2.10}
\]

\[
\frac{\partial C_i^s}{\partial t} = K_d C_i^a \frac{\partial C_i^a}{\partial t} \tag{2.11}
\]

Where \( C_i^n \) is the concentration of compound i in phase n, D is the longitudinal dispersion coefficient, v is the non-reactive transport velocity, t is time, z is the longitudinal coordinate, \( S_i \) is the pure compound aqueous solubility, \( \gamma_i^n \) is the activity coefficient of compound i in phase n, and \( K_d_i \) is the sediment-water distribution coefficient for compound i. The different phases are represented by,
"fo" for the equilibrium controlled fraction of residual oil phase ("fast oil"), "so" for the mass transfer limited fraction of the residual oil phase ("slow oil"), "a" for the aqueous phase, and "s" for the solid phase.

Borden also reported the results of experiments in which initially organic-free water was flushed through a sand-packed column containing a residual saturation of unleaded gasoline. The effluent water was then analyzed for several partially water soluble components of the gasoline. Figure 2.1 shows the results of these experiments for benzene, toluene, ethylbenzene, and meta- and para-xylene. Note that for each constituent reported, the basic shape of the effluent curve is the same, flush-out at approximately constant concentrations followed by diminishing effluent concentrations which then stabilize orders of magnitude below the initial effluent concentrations. This work was very significant, because the experiments simulate what happens in many pump-and-treat remediation efforts for gasoline spills within the subsurface.
Figure 2.1  BTEX data from Borden and Kao (1989).

In addition to measuring the effluent concentration history, Borden attempted to measure the mass transfer coefficient $k_m$, as given by equation (2.7), by an intermittent flow procedure. As might be expected, the coefficients for each of the individual components were relatively equivalent. This seems to indicate that for modeling purposes, the effective mass transfer rate only needs to be determined for one component of a multicomponent oil. The effective mass transfer coefficients reported by Borden are shown in table 2.1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$k_m$ (hr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.030</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.033</td>
</tr>
<tr>
<td>m+p-Xylene</td>
<td>0.031</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>0.012</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>0.019</td>
</tr>
</tbody>
</table>

Table 2.1  Effective Mass Transfer Rates for Individual Hydrocarbons
Borden proceeded to analyze the data utilizing the two-site numerical model. From this he concluded that the two-site modeling approach was a significant improvement over previous modeling efforts which were limited by the exclusive use of the local equilibrium assumption.

Experimental Work by Rixey et al.

Rixey, et al. (1990) have presented the results of soil flushing experiments very similar to those of Borden. The primary difference was that the columns were loaded with prepared mixtures of gasoline range hydrocarbons. The prepared mixtures provided insight into the magnitude of the effect of a single component's interdependency with other components of a multicomponent residual oil. Rixey evaluated the data by means of a simplified one-dimensional finite difference transport model which assumed instantaneous equilibrium between phases, included a functional relationship for the interdependency of the individual components, and neglected hydrodynamic dispersion. Rixey concluded that the model was useful for predicting the maximum leaching potential of residual hydrocarbons from a residual oil source, but was not capable of characterizing the tailing of the effluent concentration history curve.
Experimental Work by Miller et al.

Miller, et al. (1990) have presented the results from an evaluation of 70 column experiments which were performed to estimate mass transfer coefficients and their relationship to aqueous phase velocity, NAPL saturation, and particle diameter. In order to simplify the investigation, Miller limited his study to single component residual oils. Miller concluded that mass transfer rate coefficients were directly related to aqueous phase velocity and NAPL saturation. Miller also found no relationship between the rate coefficient and particle size.

Theoretical Work by Powers et al.

Powers, et al. (1991) have very recently presented a theoretical study of the significance of nonequilibrium dissolution of a residual oil. An analytical transport model analogous to the two-site model presented by Borden, with the exception that only a single solute is considered, has also been presented. This work is reported to be the preface for a continued effort to quantify the mass transfer limited phenomena.
Chapter 3

Evaluation of Selected Transport Models

The first objective of this research was to locate and evaluate contaminant transport models which might be applicable to modeling the dissolution of a residual oil source due to vertical infiltration of water. Four criteria governed the selection of models to evaluate. First, the model must be capable of qualitatively and quantitatively characterizing the aqueous solute concentration of an infiltrating water as it exits a zone of residual oil. Second, the model should be flexible enough to allow simple and predictable manipulation of its effluent history profile. Third, the model must be formulated in such a manner as to allow its use as a submodel to BIOPLUME II. Fourth, the model should require reasonable computational expense. These criteria were used to evaluate the analytical solutions of Parker, et al. (1984) and Wise, et al. (To Be Submitted 1991) and the numerical model of Kool, et al. (1989). Multiphase multicomponent numerical flow and transport models such as those presented by Abriola, et al. (1985) and Corapcioğlu, et al. (1987) and the multicomponent transport model presented by Borden, et al. (1989) were eliminated from consideration because they would fail the criteria for a reasonable computational expense.
**Two-Site Analytical Model for Dissolution of a Residual Oil**

**Model Development**

**Two-Site Adsorption**

Several analytic solutions and a computer code for the transport of a solute influenced by adsorption have been presented by Parker, et al. (1984). The primary purpose for developing the code was to quantify various model parameters, for example, dispersion coefficients, retardation factors, and degradation constants. The code was designed to operate in both the forward and inverse modes, that is, calculating an effluent history from given model parameters or predicting selected parameters from observed data. One solution in particular, the "Two-Site/Two-Region Non-Equilibrium Model," proved adaptable to modeling residual oil dissolution, after a transformation of certain variables was made.

The two-site non-equilibrium model was developed for the case in which adsorption is assumed to occur at two types of sites, one governed by equilibrium adsorption (type-1 sites) and the other by first-order kinetic non-equilibrium adsorption (type-2 sites). A two-site adsorption model had previously been discussed by several other authors, including Cameron, et al. (1977) and Nkedi-Kizza, et al. (1984). The general formulation of the transport equation for a single solute species during steady fluid flow in a one-dimensional homogeneous system, without the reaction terms, is described by
\[ (1 + \frac{fpK_d}{\theta_w}) \frac{\partial c}{\partial t} + \frac{\rho}{\theta_w} \frac{\partial s_2}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} \]  

(3.1)

and

\[ \frac{\partial s_2}{\partial t} = \alpha \left[ (1-f) K_d c - s_2 \right] \]  

(3.2)

where \( c \) is the aqueous phase concentration of the solute (ML\(^{-3}\)), \( s_2 \) is the type-2 site adsorbed concentration per unit mass of the solid phase (MM\(^{-1}\)), \( \rho \) is the bulk density of the porous media (ML\(^{-3}\)), \( f \) is the fraction of type-1 adsorption sites to all sites, \( K_d \) is the equilibrium partition constant (L\(^3\)M\(^{-1}\)), \( x \) is distance (L), \( t \) is time (T), \( D \) is a dispersion coefficient (L\(^2\)T\(^{-1}\)), \( v \) is the pore water velocity (LT\(^{-1}\)), \( \theta_w \) is the volumetric water content (L\(^3\)L\(^{-3}\)), and \( \alpha \) is a first order rate coefficient (T\(^{-1}\)). The initial condition is given by,

\[ c(x,0) = c_i \]  

(3.3)

where \( c_i \) is the initial concentration (ML\(^{-3}\)), and the boundary conditions are given by,

\[ \left( c - \frac{D}{v} \frac{\partial c}{\partial x} \right) \bigg|_{x=0} = c_{in}(t) \quad \text{, at the inlet} \]  

(3.4)

\[ \frac{\partial c}{\partial x} (\infty,t) = \text{finite} \quad \text{, at the exit} \]  

(3.5)

Equations (3.1) and (3.2) were reformulated with dimensionless parameters. The result is the following,

\[ \beta R \frac{\partial c_1}{\partial T} + (1-\beta) R \frac{\partial c_2}{\partial T} = \frac{1}{P} \frac{\partial^2 c_1}{\partial z^2} - \frac{\partial c_1}{\partial z} \]  

(3.6)
and \((1-\beta) R \frac{\partial c_2}{\partial T} = \omega (c_1 - c_2)\) \hspace{1cm} (3.7)

The dimensionless parameters are defined as;

\[
z = \frac{x}{L}, \quad T = \frac{v t}{L}, \quad P = \frac{v L}{D},
\]

\[
R = 1 + \frac{\rho K_d}{\theta_w}
\] \hspace{1cm} (3.8)

\[
\beta = \frac{\theta_w + f \rho K_d}{\theta_w + \rho K_d}
\] \hspace{1cm} (3.9)

\[
\omega = \alpha (1-\beta) R \frac{L}{v}
\] \hspace{1cm} (3.10)

\[
c_1 = \frac{c - c_i}{c_o - c_i}
\] \hspace{1cm} (3.11)

\[
c_2 = \frac{s_2 - (1-f) K_d c_i}{(1-f) K_d (c_o - c_i)}
\] \hspace{1cm} (3.12)

Where \(L\) is the length of the system \((L)\), \(c_o\) is the concentration of the inlet solution \((ML^{-3})\), and \(c_i\) is the uniform initial concentration \((ML^{-3})\). The derivation of the solution to equations (3.6) and (3.7) is not presented by Parker but has been presented by others, including Cameron, et al. (1977).

**Two-Site Dissolution**

A similar problem to that of adsorption, is the transport of a solute which is introduced to the aqueous phase through the process of dissolution from a residual oil source. Furthermore, dissolution
from a residual oil source can also be assumed to occur at two types of sites, one governed by equilibrium (or near equilibrium) dissolution (type-1 sites) and the other by first-order kinetic non-equilibrium dissolution (type-2 sites). A one-dimensional numerical model for two-site dissolution of a residual oil has recently been presented by Borden, et al. (1989). Borden described the type-1 and type-2 sites and "fast oil" and "slow oil", respectively. Figure 3.1 is a schematic representation of "fast" and "slow" oil.

![Schematic representation of a residual oil for the two-site model.](image)

Figure 3.1 Schematic representation of a residual oil for the two-site model.

The formulation of equations and the transformation of variables for the two-site analytical model for dissolution are presented here. The formulation of the transport equation, which is similar to that presented for two-site adsorption, is for a single solute
species during steady fluid flow in a one-dimensional homogeneous system. The equation, neglecting production and decay terms, is described by,

\[ \theta_w \frac{\partial c}{\partial t} + \theta_{fo} \frac{\partial c_{fo}}{\partial t} + \theta_{so} \frac{\partial c_{so}}{\partial t} + \rho \frac{\partial s}{\partial t} = \theta_w D \frac{\partial^2 c}{\partial x^2} - \theta_w v \frac{\partial c}{\partial x} \]  

(3.13)

Furthermore, at equilibrium,

\[ c_{fo} = c_{so} = K c \quad \text{and} \quad s = K_d c \]

where, \(c\) is the aqueous phase concentration (ML\(^{-3}\)), \(c_{fo}\) is the concentration of the fast oil fraction (ML\(^{-3}\)), \(c_{so}\) is the concentration of the slow oil fraction (ML\(^{-3}\)), \(K\) is the equilibrium oil/water partition coefficient for the solute, and the other variables are as previously defined for two-site adsorption.

For the fast fraction, \(\frac{\partial c_{fo}}{\partial t} = K \frac{\partial c}{\partial t}\)  

(3.14)

For the slow fraction, \(\frac{\partial c_{so}}{\partial t} = \alpha [K c - c_{so}]\)  

(3.15)

For the adsorbed fraction, \(\frac{\partial s}{\partial t} = K_d \frac{\partial c}{\partial t}\)  

(3.16)

where \(s\) is the adsorbed concentration per unit mass of the solid phase (MM\(^{-1}\)), and \(K_d\) is as previously defined. Next we consider

\[ \theta_{fo} = f \theta_o \quad \text{and} \quad \theta_{so} = (1-f) \theta_o \]
where \( f \) is the fraction of residual oil governed by equilibrium (or near equilibrium) dissolution. This leads to,
\[
\frac{\partial c}{\partial t} + \frac{f}{\theta_w} \frac{\partial c_{fo}}{\partial t} + \frac{(1-f)\theta_o}{\theta_w} \frac{\partial c_{so}}{\partial t} + \frac{\rho s}{\theta_w} \frac{\partial s}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} \tag{3.17}
\]

After substitution we have,
\[
(1 + \frac{f}{\theta_w} \frac{\theta_o K}{\theta_w} + \frac{\rho K_d}{\theta_w}) \frac{\partial c}{\partial t} + \frac{(1-f)\theta_o}{\theta_w} \frac{\partial c_{so}}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} \tag{3.18}
\]

In a similar manner to the method for two-site adsorption, dimensionless parameters can be defined as,
\[
z = \frac{x}{L}, \quad T = \frac{v t}{L}, \quad P = \frac{v L}{D}
\]

which leads to the following,
\[
(1 + \frac{f}{\theta_w} \frac{\theta_o K}{\theta_w} + \frac{\rho K_d}{\theta_w}) \frac{\partial c}{\partial T} + \frac{(1-f)\theta_o}{\theta_w} \frac{\partial c_{so}}{\partial T} = \frac{1}{P} \frac{\partial^2 c}{\partial z^2} - \frac{\partial c}{\partial z} \tag{3.19}
\]

Furthermore, the dimensionless parameters defined by equations (3.8) through (3.12) can be redefined as,
\[
R = 1 + \frac{\theta_o K}{\theta_w} + \frac{\rho K_d}{\theta_w} \tag{3.20}
\]
\[
\beta = \frac{\theta_w + f \theta_o K + \rho K_d}{\theta_w + \theta_o K + \rho K_d} \tag{3.21}
\]
\[
\omega = \alpha (1-\beta) R \frac{L}{v} \tag{3.22}
\]
\[
\begin{align*}
    c_1 &= \frac{c - c_i}{c_o - c_i} \quad \Rightarrow \quad \frac{\partial c}{\partial T} = (c_o - c_i) \frac{\partial c_1}{\partial T} \quad (3.23) \\
    c_2 &= \frac{c_{so} - K c_i}{K (c_o - c_i)} \quad \Rightarrow \quad \frac{\partial c_{so}}{\partial T} = K (c_o - c_i) \frac{\partial c_2}{\partial T} \quad (3.24)
\end{align*}
\]

The proceeding dimensionless parameters lead to the following,

\[
\beta R \frac{\partial c_1}{\partial T} + (1-\beta) R \frac{\partial c_2}{\partial T} = \frac{1}{P} \frac{\partial^2 c_1}{\partial z^2} - \frac{\partial c_1}{\partial z} \quad (3.25)
\]

and \( (1-\beta) R \frac{\partial c_2}{\partial T} = \omega (c_1 - c_2) \) \quad (3.26)

Equations (3.25) and (3.26) are identical to equations (3.6) and (3.7). Therefore, it possible to use the code developed for two-site adsorption to solve the similar problem of solute dissolution.

**Model Capability**

The capability of the two-site model to describe the dissolution of BTEX components from a residual oil has been demonstrated as follows. First, the model was evaluated for its dependency on certain input parameters. Second, the model was evaluated for its ability to fit experimental data. Third, the model was evaluated for its ability to predict results from independently determined input parameters.

**Model Dependency on Input Parameters**

In order to fully understand results obtained from the two-site model, it is necessary to further define some of the dependent
variables. The variables which need further discussion are $R$, $K_d$, $f$, $\beta$, and $\alpha$.

The dimensionless parameter $R$, as defined by equation (3.20), relates the total concentration of a solute in the system to the solute concentration in the aqueous phase. Another way to define $R$ is to relate it to the total mass of the solute in the system as follows,

$$ R = \frac{\text{Total Mass}}{C_w \times \text{Pore Volume}} \quad (3.27) $$

For most cases of dissolution from a residual oil, the value of $R$ will typically be dominated by the concentration of the solute in the residual oil phase. For example, for the column experiments reported by Borden, the term associated with the residual oil, $\frac{\theta_o K}{\theta_w}$, was 99.4% of the value of $R$. The value of $R$ was calculated from equation (3.20) to equal 156.7, and from equation (3.27) to equal 169.6. The discrepancy is due to inaccuracies in determining system parameters.

The variable $K_d$, is the equilibrium partition constant (L$^3$M$^{-1}$) which relates the adsorbed concentration of the solute in the solid phase to the aqueous concentration. The formulation of the two-site model for dissolution of a solute from a residual oil, limits the adsorption partitioning relationship to a linear isotherm of the form $s = K_d c$. Additionally, only type-1 sites are considered. However, the limitations imposed on the model, by the assumed adsorption mechanism, should not impose a significant limitation on the
capability of the model for typical circumstances. This is because in
the presence of a residual oil, the aqueous concentration will
typically be dominated by the dissolution process as previously
described. For example, for the column experiments reported by
Borden, the term associated with the solid phase, \( \frac{\rho K_d}{\theta_w} \), was 0.01% of
the value of R. The dependence of the model on \( K_d \) is shown
graphically in figure 3.2, where the reported value of \( K_d \) for the
component toluene, 0.018, is compared with an arbitrarily set value
of 18.0. It is apparent from figure 3.2, that increasing \( K_d \) will shift
the effluent curve in the direction of increasing time, by an amount
which will make the mass associated with the area between the two
curves equal to the mass added to the system. Note that the value
for \( K_d \), 0.018, is actually the value for \( \frac{\rho K_d}{\theta_w} \), as reported by Borden, et
al. (1989). Also note that mass is added to the system for the greater
value of \( K_d \), because the initial aqueous concentration was assumed
to have the same value for both cases.
Figure 3.2 Two-site model dependency on $K_d$, the solid phase equilibrium adsorption coefficient.

The variable $f$, as previously defined, is the fraction of residual oil governed by equilibrium (or near equilibrium) dissolution. This variable is related primarily to the distribution of the residual oil within a system, which in turn is related to the various properties of the media and the fluid phases present, for example, the pore size distribution and the wettability of the medium. Borden pointed out that the value of $f$ could be inferred from a determination of the mass of a component remaining in the column after a solute has been removed from the type-1 sites. For the component toluene, $f$ could be inferred to be 0.90, as 10% of the initial mass of toluene remained in the column at the conclusion of the experiment. The dependence of the model on $f$ is shown graphically in figure 3.3, where the
reported value of $f=0.90$, is compared versus an arbitrarily set value of 0.98. It is apparent from figure 3.3, that decreasing $f$ will redistribute mass from later times to earlier times. Note that the "tail" of the effluent history curve is simply shifted up in order to accommodate the additional mass. This is because the mass transfer coefficient is assumed to remain constant. However, the mass transfer coefficient is not likely to be constant in real systems. In real systems, it is reasonable to expect that the tail will also flatten due to the presence of larger globules which might have lower mass transfer coefficients.

![Figure 3.3](image.png)

Figure 3.3 Two-site model dependency on $f$, the fraction of fast oil sites.

The dimensionless parameter $\beta$ is a function of the parameter $R$ and the variable $f$. The parameter $\beta$, like $R$, is also influenced by the dominance of the residual oil phase solute concentration. Typically,
for the case of two-site dissolution from a residual oil, $\beta$ will approximate $f$ due to the fact that $\theta_o K$ and $f\theta_o K = \theta_w + \rho K_d$. For the column experiments reported by Borden, $\beta$ was calculated to be 0.9007 when $f$ was assumed to equal 0.9000.

The variable $\alpha$, is a first-order rate coefficient ($T^{-1}$) associated with the type-2 sites. The variable $\alpha$ can be further defined by the following expression,

$$\alpha = K_m \frac{a_{so}}{V_o} \quad (3.28)$$

where, $K_m$ is a mass transfer constant for the solute in the oil ($LT^{-1}$), $a_{so}$ is the oil/water interfacial surface area ($L^2$), and $V_o$ is the volume of the oil globule ($L^3$). For the column experiments reported by Borden, $\alpha$ was determined by an intermittent flow procedure to equal 0.03 hr$^{-1}$. The dependence of the model on $\alpha$ is shown graphically in figure 3.4, where a value of $\alpha$=0.0018 hr$^{-1}$, is compared with a value of twice its magnitude, 0.0035 hr$^{-1}$. It is apparent from figure 3.4, that decreasing $\alpha$ flattens the slope of the tail of the effluent history curve. One of the primary limitations of the two-site model, particularly as applied to dissolution, is that every globule of residual oil in a system must be grouped into one of only two types of sites. This requires the assumption that the type-2 non-equilibrium sites all possess the same value for $\alpha$. However, in reality there is a continuum of non-equilibrium type sites which have a range of $\alpha$ values. Furthermore, the value of $\alpha$ for a given oil
globule is not constant through time. This is because $K_m$ may decrease and the ratio of $a_{so}$ to $V_o$ will increase as the oil weathers.

```
Model Parameters:
pore velocity = 300.0 cm/d
Dispersivity = 0.1 cm
R = 149.2
f (fast oil) = 0.98
Kd (sorbed) = 0.018
```

Figure 3.4 Two-site model dependency on $\alpha$, the first order rate coefficient.

Two other variables which have a significant effect on the character of the effluent history curve for dissolution of a residual oil are the average pore water velocity and the dispersion coefficient. The average pore water velocity for the experiments reported by Borden, was 300. cm/d. Figure 3.5 compares the effluent history curve for the component toluene with $v$ equal 150., 300., and 600. cm/d. The reported dispersivity ranged between 0.1 and 0.2 cm. Figure 3.6 compares the reported value of dispersivity to the extreme example of negligible dispersivity.
Figure 3.5 Two-site model dependency on $v$, the average pore water velocity.

Figure 3.6 Two-site model dependency on $D$, the dispersion coefficient. Experimental data from Borden, et al. (1989).
Two-Site Model Fit to Experimental Data

The two-site model was applied, in the inverse mode, to the experimental data reported by Borden. Each of the model runs presented here were for the component toluene. The objective was to evaluate the flexibility of the model to fit data and to evaluate the applicability of the two-site theory to dissolution from a residual oil. The evaluation began by fitting the data to the maximum number of input parameters allowed by Parker's code. The code was capable of fitting four of the five required input parameters simultaneously. The five input parameters are: $v$, $D$, $R$, $\beta$, and $\omega$. The variable $v$ was well defined for the experiment, therefore, it was held constant throughout the fitting procedures. Table 3.1, presented at the end of this section, summarizes the various model runs and some associated statistical results. A discussion of the statistical results is also presented at the end of this section.

In the inverse mode, that is, when fitting data, the objective of the fitting procedure is to minimize the sum of the squared residuals as follows,

$$
\text{minimize} \quad \text{SSQ} = \sum_{i=1}^{\text{NOB}} R(i)^2
$$

$$
R(i) = Wt \times (C(i) - F(i))
$$

$$
Wt = 1.0 \quad \text{or} \quad \frac{1}{C(i)}
$$
where SSQ is the sum of the squared residuals, NOB is the number of observations, R(i) is the residual concentration, C(i) is the observed concentration, F(i) is the calculated concentration for a given set of model input parameters, and Wt is a weighting function. The minimization is carried out iteratively by the Levenberg-Marquardt method (Marquardt, 1963). Sometimes it is necessary to weight the residuals when the experimental data range over several orders of magnitude, which the Borden data do. A common weighting function used is \( \frac{1}{C(i)} \), which results in an increased weighting for smaller observed concentrations. For application of the two-site model, weighting the residuals in this way consistently produced a better fit to the data.

Figure 3.7 is the resulting effluent history curve for fitting four input parameters simultaneously. It is quite apparent that the model is certainly flexible enough to fit experimental data.
The next step was to fit three parameters simultaneously. Figure 3.8 is the resulting effluent history curve with the variable D held constant. The failure to fit the tail of the curve is the result of using unweighted residuals. The result, however, is interesting in that the fitted value of R is 148.1. Considering that the value of R was determined essentially for only the fast oil, since the tail was neglected, then R divided by 0.90 should be an indication of the true value of R, the result is 164.5, which compares favorably to the values calculated from equations (3.20) and (3.27).
Figure 3.8 Three fitted parameters. Two-site model fit to soil column data.

Figure 3.9 is the resulting effluent history curve with the variable R held constant. R was held constant at 148.0 because this value tended to produce better fits for most model runs. Furthermore, it can be justified quantitatively when consideration is taken for the experimental mass balance error. Borden reported that 76% of the mass was accounted for in the effluent water, 10% remained in the column, and 14% was unaccounted for. Taking the unaccounted for mass into consideration, R could be as low as 145.9. R could be even lower if inaccuracies in measurement are considered. Nevertheless, it is apparent from figure 3.9 that the data can be fit quite well with three fitted parameters. It should be noted that the fitted value of $\omega=0.0054$ corresponds to a calculated value for $\alpha$ of
0.0012 hr\(^{-1}\), far less than the independently determined value of 0.03 hr\(^{-1}\).

Figure 3.9 Three fitted parameters. Two-site model fit to soil column data.

The next step was to fit two parameters simultaneously. Figure 3.10 is the resulting effluent history curve with the variables R and D held constant. It is apparent that the model is still capable of fitting the most significant characteristics of the effluent curve. Note that the fitted value for \(\beta\), which essentially should equal the fraction of fast sites, is 0.979. This is considerably greater than that expected considering the amount of mass remaining in the column at the conclusion of the experiment. Also note that the fitted value of \(\omega=0.0076\) corresponds to a calculated value for \(\alpha\) of 0.0017 hr\(^{-1}\).
Figure 3.10 Two fitted parameters. Two-site model fit to soil column data.

The final step was to fit one parameter. Figure 3.11 is the resulting effluent history curve with the variables R, D, and β held constant. Note that with the larger fraction of slow oil, the tail of the effluent curve is forced to be very flat. This is most likely the result of the model's limitation to only two types of sites. Had the model been able to include intermediate type sites, the curve would not have fallen below the experimental data in the range of 150 to 450 pore volumes, and less mass would have been associated with the tail of the curve.
Figure 3.11 One fitted parameter. Two-site model fit to soil column data.

Table 3.1 is a summary of results for the various model runs. In addition to fitting selected parameters, the Parker code calculates the upper and lower 95% confidence intervals and a t-value. The absolute difference between the upper (or lower) 95% confidence interval and the fitted value is presented in table 3.1 as Δ95% CI. This is a measure of the variance of the fitted value. The tighter the confidence interval, the greater the confidence in the fitted value, that is, assuming the known values are accurate. Therefore, a comparison of the difference between runs is a relative indication of the improved confidence gained by fitting fewer parameters. The t-value is a measure of the independence of a parameter. For this reason a t-value is not calculated when only one parameter is fit.
<table>
<thead>
<tr>
<th>Run No.</th>
<th>Fig. No.</th>
<th>Parms Fitted</th>
<th>Parm</th>
<th>Fixed Value</th>
<th>Fitted Value</th>
<th>Δ95% CI</th>
<th>t-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.7</td>
<td>4</td>
<td>D</td>
<td>206.</td>
<td>34.9</td>
<td>11.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>R</td>
<td>134.</td>
<td>5.23</td>
<td>51.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<td>0.0018</td>
<td>1103.</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>ω</td>
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<td>0.0010</td>
<td>10.3</td>
<td></td>
</tr>
<tr>
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<td>Not 3</td>
<td>D 30.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Shown</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>R</td>
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<td>71.1</td>
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<td></td>
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<td>0.0024</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ω</td>
<td>0.0076</td>
<td>0.0023</td>
<td>6.70</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3.8</td>
<td>3 30.</td>
<td>D</td>
<td>148.</td>
<td>6.72</td>
<td>43.9</td>
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</tr>
<tr>
<td></td>
<td>(Unweighted)</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>R</td>
<td>148.</td>
<td>6.72</td>
<td>43.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>β</td>
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<td></td>
</tr>
<tr>
<td>4</td>
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<td>3 30.</td>
<td>D</td>
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<td></td>
</tr>
<tr>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>β</td>
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</tr>
<tr>
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<td></td>
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<td>ω</td>
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</tr>
<tr>
<td>5</td>
<td>3.10</td>
<td>2 30.</td>
<td>D</td>
<td>148.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>R</td>
<td>148.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>β</td>
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<td>0.0024</td>
<td>828.</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ω</td>
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<td>0.0023</td>
<td>6.72</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>3.11</td>
<td>1 30.</td>
<td>D</td>
<td>148.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>R</td>
<td>148.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>β</td>
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<td>0.0005</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Not 1</td>
<td>D 30.</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Shown</td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>R</td>
<td>148.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>β</td>
<td>0.979</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ω</td>
<td>0.0075</td>
<td>0.0022</td>
<td>--</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.1 Summary of results for two-site model fit to soil column data.
The following observations have been made based on the statistical results presented in table 3.1.

1. Comparing Runs No. 1 and No. 4, it appears that fixing the parameter R significantly increases the confidence in the parameter D, but not Beta and Omega.

2. Comparing Runs No. 1 and No. 2, it appears that fixing the parameter D slightly increases the confidence in the parameter R, but also slightly decreases the confidence in the parameters Beta and Omega. It also appears that this increases the independence of Beta and Omega.

3. Comparing Run No. 5 to Runs No. 2 and No. 4, it appears that fixing the parameters D and R do little to change the confidence or independence of the parameters Beta and Omega.

4. Comparing Runs No. 6 and No. 7, it appears that the confidence in the parameter Omega is directly related to the accuracy of Beta.

5. Comparing Runs No. 3 and No. 2, it appears that fitting data utilizing unweighted residuals results in a poor estimation of the parameter Omega.
Two-Site Model Run with Independently Determined Input Parameters

The two-site model was applied using the independently determined input parameters reported by Borden and an R value of 148.1. Figure 3.12 is the resulting effluent curve. It is obvious that the model has failed to fit the tail of the curve with the reported parameters. However, it is interesting that the model compares well with the most significant part of the curve (that is, significant as a contamination source). It is uncertain why the mass transfer coefficient measured in the lab does not produce the tail characteristic. One explanation may be a result of the distribution of the type-2 sites in the column. The model assumes that the type-2 sites are homogeneously distributed throughout the system. However, a homogeneous distribution is very unlikely for a residual oil. In the event the tail of the effluent curve was a result of a few type-2 sites located near the exit of the column, as Borden's data indicates it might, then the driving force of equation (3.15), \([Kc - c_{50}]\), would have been greater than expected as \(c\) would have been lower as it contacted the type-2 sites. Assuming a weaker driving force would have resulted in a greater calculated value of \(\alpha\) in order to produce the same rate of dissolution. Another explanation may be the decoupling of equations, although this would seem unlikely for the component toluene since it is one of the most soluble components in the residual oil.
Figure 3.12 Independently determined parameters. Two-site model applied to soil column data.

The two-site model was also applied using an average pore water velocity that might be encountered in a real field situation. The velocity was estimated from that which would result from 12.0 inches of rainfall per year (that is, rainfall that actually infiltrates). The other input parameters were the independently determined parameters reported by Borden with the exception of $\alpha$ which was taken as 0.0017 hr$^{-1}$ to be conservative. Figure 3.13 is the resulting effluent curve. It is interesting that the type-2 sites have little effect at the lower velocity even with the small value for $\alpha$. This places the greatest significance on determining the value of $R$, the total mass in the system.
Figure 3.13  Typical average pore water velocity for vertical infiltration. Two-site model compared to soil column data.

The Two-Site Model as a Submodel

The two-site model includes the dominant physical processes which control the dissolution of a residual oil and the subsequent transport of the solute. This is a significant advantage over the other two models evaluated here. Furthermore, the two-site model is the most flexible model for fitting experimental data.

The primary disadvantage of the two-site model is that it may be difficult to include first-order decay of the solute. However, solutions for the two-site model with decay have been presented by Lassey (1988), Lindstrom (1976), and van Genuchten, et al. (1989). A limitation of the two-site model is that it may be difficult to accurately determine the parameters β and ω.
Apparent Partitioning Model for Dissolution of a Residual Oil Source

The model presented by Wise, et al. (To Be Submitted 1991), is a simple model intended to characterize the time-variant effluent concentration history of a residual oil source. This is accomplished by employing a non-linear "apparent partitioning" of the more soluble components in a similar manner as Valocchi (1984) employed an "effective $K_d$" for adsorption. The apparent partitioning model was developed by neglecting the processes of dispersion, sorption, reaction, and kinetics in favor of a non-linear apparent partitioning relationship. It is important to note that this results in a model that is phenomenological in nature.

Model Development

The mathematical basis of the model presented by Wise, et al. (To Be Submitted 1991), is a method of characteristics solution of the general one-dimensional transport equation, neglecting the processes of dispersion, sorption, reaction, and kinetics in favor of an apparent non-linear partitioning of the partially soluble residual oil components. Assuming steady flow ($dq/dt=0$) and local equilibrium, one obtains the following transport equation:

$$
\theta_w \left[ 1 + \frac{\theta_o}{\theta_w} \frac{\partial c_o}{\partial c_w} \right] \frac{\partial c_w}{\partial t} + q \frac{\partial c_w}{\partial z} = 0
$$

(3.29)
Where, $\theta_w$ and $\theta_o$ are the moisture and oil contents of the porous medium, respectively, $c_w$ and $c_o$ are the aqueous and oil phase concentrations (ML$^{-3}$), respectively, $q$ is the darcy velocity ($\nu \theta_w$) (LT$^{-1}$), and $z$ is the distance along a streamline (L).

The transport equation, nondimensionalized for time in terms of pore volumes, can be rewritten as follows,

$$
\frac{q}{\zeta} \left[ 1 + \Theta \frac{\partial c_o}{\partial c_w} \right] \frac{\partial c_w}{\partial \tau} + q \frac{\partial c_w}{\partial z} = 0
$$

(3.30)

Where, $\zeta$ is the thickness of the oil layer (L), $\tau$ is the number of pore volumes swept through the oil layer, and $\Theta$ is an equivalent oil-water content ratio, which can be further defined by,

$$
\Theta = \frac{1}{\zeta} \int_{0}^{\zeta} \frac{\theta_o(z)}{\theta_w(z)} \, dz
$$

(3.31)

The apparent partitioning model is developed subject to the initial conditions,

$$
c_o(0,z) = ic_o \quad \forall \ 0 \leq z \leq \zeta
$$

$$
c_o(0,z) = 0 \quad \forall \ z > \zeta
$$

and the boundary condition,

$$
c_w(\tau,0) = 0 \quad \forall \ \tau \geq 0
$$
A method of characteristics solution results in the simple and shock wave expressions,

\[
\frac{dz}{d\tau} = \zeta \left[ 1 + \Theta \frac{\partial c_o}{\partial c_w} \right]^{-1} \tag{3.32}
\]

\[
\frac{dz}{d\tau} = \zeta \left[ 1 + \Theta \frac{\Delta c_o}{\Delta c_w} \right]^{-1} \tag{3.33}
\]

**Solution for a Modified Freundlich Apparent Partitioning Relationship**

A modified Freundlich relationship has been employed to describe the apparent non-linear partitioning of a hydrocarbon component between the oil and water phases. It is important to note that this is an empirical relationship and it is not intended to describe a true partitioning. Figure 3.14 is a schematic representation of the modified partitioning relationship.

![Diagram](image)

Figure 3.14 Schematic of the modified Freundlich apparent partitioning relationship.
The apparent partitioning can be described as follows:

\[ c_0 = \gamma(c_W) \delta \quad \forall \quad b c_o \leq c_0 \leq i c_o \]  \hspace{1cm} (3.34)

\[ c_0 = \kappa c_W \quad \forall \quad 0 \leq c_0 \leq b c_o \]  \hspace{1cm} (3.35)

where, \( \delta \) and \( \gamma \) are empirical, dimensionless parameters, and \((b c_w, b c_o)\) is referred to as the breakpoint composition, below which the partitioning becomes linear. The non-linearity of (3.34) produces a method of characteristics solution which is a spreading wave of constant concentrations as depicted in figure 3.15. It is the spreading wave that characterizes the effluent concentration history curve between the times \( i \tau_p \) and \( b \tau_p \). The spreading wave is primarily a result of dispersion and kinetic mass transfer limitations. The linear relationship of (3.35) is necessary in order to characterize the tail of the effluent history curve which is also primarily a result of kinetic mass transfer limitations.

Figure 3.15    Resultant method of characteristics solution
Figure 3.16 is a schematic of the effluent concentration history at the far extent of the oil layer assuming a modified Freundlich apparent partitioning of the residual oil. In relation to figure 3.15, figure 3.16 is a cross section taken along the horizontal dotted line drawn at $z = \zeta$.

Figure 3.16  Effluent Concentration History Schematic

Equations (3.32), (3.34), and (3.35) together describe the effluent concentration history with the following expressions,

\[
c_w(\tau, \zeta) = \begin{cases} 
  i_{c_w} & \forall \quad 0 \leq \tau \leq i_{\tau_p} \\
  \left( \frac{(\tau-1)}{\Theta \gamma \delta(i_{c_w})} \right)^{\delta-1} & \forall \quad i_{\tau_p} < \tau < b_{\tau_p} \\
  b_{c_w} & \forall \quad b_{\tau_p} \leq \tau \leq 0_{\tau_p}
\end{cases}
\]  

(3.36)

where

\[
i_{\tau_p} = 1 + \Theta \gamma \delta(i_{c_w})^{-1}
\]  

(3.37)

\[
c_w(\tau, \zeta) = \left\{ \begin{array}{ll}
  \frac{1}{\Theta \gamma \delta} & \forall \quad i_{\tau_p} < \tau < b_{\tau_p} \\
  b_{c_w} & \forall \quad b_{\tau_p} \leq \tau \leq 0_{\tau_p}
\end{array} \right.
\]  

(3.38)

where,

\[
b_{\tau_p} = 1 + \Theta \gamma \delta(b_{c_w})^{-1}
\]  

(3.39)
where \[ 0_{\tau_p} = 1 + \Theta \gamma (b c_w)^{\delta-1} \quad (3.41) \]
\[ c_w(\tau, \zeta) = 0 \quad \forall \quad \tau > 0_{\tau_p} \quad (3.42) \]

Model Capability

The capability of the apparent partitioning model was evaluated by applying it in the inverse mode to the data reported by Borden. Figure 3.17 shows the model fit to the experimental data for the component toluene. It is apparent that the model is flexible enough to adequately fit data. However, the model is not applicable to predicting the effluent concentration history in the forward mode without first being calibrated to soil column data or a more sophisticated model.

![Graph showing model parameters and fit to experimental data](image)

**Figure 3.17** Apparent partitioning model for the dissolution of toluene from a residual oil source.
The model was also applied to the other BTEX components reported by Borden. The model was capable of fitting the data of the other components equally as well as it fit the data for toluene. The parameters estimated for each of the BTEX components are listed in table 3.2.

<table>
<thead>
<tr>
<th>Component</th>
<th>$\gamma$</th>
<th>$\delta$</th>
<th>$i_{cw}$ mg/l</th>
<th>$b_{cw}$ mg/l</th>
<th>Aqueous Solubility mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
<td>554.</td>
<td>.76</td>
<td>22.99</td>
<td>.010</td>
<td>1780.</td>
</tr>
<tr>
<td>toluene</td>
<td>2044.</td>
<td>.80</td>
<td>40.73</td>
<td>.067</td>
<td>515.</td>
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<tr>
<td>ethylbenzene</td>
<td>2876.</td>
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<td>2.91</td>
<td>.002</td>
<td>152.</td>
</tr>
<tr>
<td>m+p-xylene</td>
<td>2829.</td>
<td>.91</td>
<td>13.12</td>
<td>.041</td>
<td>198.</td>
</tr>
<tr>
<td></td>
<td>3317.</td>
<td>.91</td>
<td>1.03</td>
<td>.041</td>
<td>162.</td>
</tr>
<tr>
<td>o-xylene</td>
<td>3000.</td>
<td>.90</td>
<td>4.49</td>
<td>.003</td>
<td>175.</td>
</tr>
</tbody>
</table>

Table 3.2  BTEX model parameters for apparent partitioning model fit to Borden, et al. (1989) data.

It is interesting to note that the apparent non-linearity of the partitioning relationship appears to be proportional to the pure phase aqueous solubility of the compound. This is a reasonable result considering that the wave speed of the equilibrium aqueous phase concentration is directly proportional to the pure phase aqueous solubility. This is evident for the near equilibrium controlled sites (type-1 sites) by the following formulations:

At equilibrium,
\[ c_o = K c_w \quad \text{and} \quad \frac{\partial c_o}{\partial c_w} = K \]

and from the dimensional form of (3.31),

\[
\frac{dz}{dt} = \frac{a}{\theta_w} \left[ 1 + \frac{\theta_o}{\theta_w} \frac{\partial c_o}{\partial c_w} \right]^{-1}
\]

and this leads to,

\[
\frac{dz}{dt} = \frac{a}{\theta_w} \left[ 1 + \frac{\theta_o}{\theta_w} K \right]^{-1}
\] (3.43)

The variable \( K \) is the equilibrium partition coefficient for the oil/water mixture and is inversely proportional to the pure phase aqueous solubility. The wave speed of the initial aqueous concentration for the components benzene, toluene, and m+p-xylene have been estimated from (3.43) to be 5.6, 1.8, and 0.7 cm/d, respectively. The faster wave speed results in a faster flushout time, \( t_f \), for the equilibrium controlled sites. The faster flushout time results in a greater fraction of the initial concentration of the more soluble component remaining in the kinetic mass transfer limited sites at time \( t_f \). The fraction remaining then produces the apparent non-linearity of the effluent concentration history curve.

**Apparent Partitioning Model as a Submodel**

The apparent partitioning model has advantages and disadvantages as a submodel. The primary advantages are that it is
simple to understand and to implement. This is a result of the method of characteristics solution which produces an analytical solution. It also has the advantage that it is flexible enough to adequately characterize the effluent concentration history curve given that it can be calibrated to soil column data or a more sophisticated model. Furthermore, of the three models reviewed in this work, it requires the least computational effort.

The primary disadvantage of the apparent partitioning model is that it is phenomenological in nature, and is not appropriate for predicting the dissolution of a component from a multicomponent residual oil source without prior calibration.
**One-Dimensional Numerical Model for Dissolution of a Residual Oil**

A one-dimensional numerical model for the analysis of breakthrough curves for cation exchange under constant ionic strength was presented by Kool, et al. (1989). This model allows for fitting various isotherms to soil column data in order to estimate cation exchange capacity and exchange selectivity coefficients. The model has been modified in order to investigate the problem of dissolution of slightly soluble components from a residual oil to a mobile aqueous phase.

**Model Development**

**Development for Adsorption**

The transport equation employed by Kool is for one-dimensional solute transport under steady state flow conditions,

\[
(1 + \frac{\rho}{\theta_w} F) \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x}
\]  

(3.44)

The initial condition is given by,

\[c(x,0) = c_i\]  

(3.45)

The boundary conditions are given by,

\[c(0,t) = c_{in}(t) \quad , \text{at the inlet}\]  

(3.46)
\[
\frac{\partial c}{\partial x}(L,t) = 0 \quad \text{at the exit} \quad (3.47)
\]

The variables are defined as follows: \( c \) is the aqueous phase concentration of the solute (\( ML^{-3} \)), \( c_i \) is the initial concentration (\( ML^{-3} \)), \( \rho \) is the bulk density of the porous media (\( ML^{-3} \)), \( x \) is distance (\( L \)), \( t \) is time (\( T \)), \( D \) is a dispersion coefficient (\( L^2 T^{-1} \)), \( v \) is the pore water velocity (\( LT^{-1} \)), \( \theta_w \) is the volumetric water content (\( L^3 L^{-3} \)), and \( F = \frac{\partial s}{\partial t} \), which is the slope of the adsorption isotherm, where \( s \) is the adsorbed concentration per unit mass of the solid phase (\( MM^{-1} \)). The model's code was set up so that the slope of the adsorption isotherm was user selectable, depending on the type of exchange reaction to be evaluated.

**Development for Dissolution**

The solution technique for adsorption was modified for analyzing the problem of dissolution by replacing the adsorption isotherms with apparent partitioning relationships. The transformed transport equation is given by,

\[
(1 + \frac{\theta_a}{\theta_w} F) \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} \quad (3.48)
\]

This resulted in a similar model to that presented by Wise, et al. (To Be Submitted 1991) with the exception that dispersion can be accounted for in the transport equation. The relationships which replaced the adsorption isotherms are given by,
\[
\frac{\partial c_o}{\partial c_w} = AK
\]
, a linear relationship where AK is an equilibrium partitioning constant,

\[
\frac{\partial c_o}{\partial c_w} = ST \times AK \times c_w^{ST-1}
\]
, a Freundlich relationship where AK is a Freundlich coefficient and ST is a Freundlich exponent,

\[
\text{and} \quad \frac{\partial c_o}{\partial c_w} = \frac{ST \times AK}{(ST + c_w)^2}
\]
, a Langmuir relationship where AK and ST are a capacity and a selectivity coefficient, respectively. Each of these relationships assume the local equilibrium assumption is valid. In addition, this solution is for a single solute species only, just as the two-site and apparent partitioning models.

In addition to the isotherm modifications, the code was modified to allow for a weighting function to be applied to the residuals. This was done in a similar manner as for the two-site model.

Model Capability

The capability of the model to describe the dissolution of BTEX components from a residual oil has been demonstrated as follows. First, the model was used to compare each of the apparent partitioning relationships and its ability to fit experimental data. Second, the model was evaluated for its ability to predict results from independently determined input parameters.
Model Fit to Linear, Freundlich, and Langmuir Partitioning Relationships

The linear relationship is the only one included in the modified Kool model which is a true partitioning relationship for the dissolution of the slightly soluble components from a residual oil. This model, used with the linear relationship, is different from the two-site model in that only type-1 sites are considered. Figure 3.18 compares the two solutions for identical input parameters.

![Diagram showing model parameters and comparison of solutions]

Figure 3.18  Modified Kool model with a linear partitioning relationship compared to the two-site model for the dissolution of toluene.

It is apparent from figure 3.18 that there is acceptable agreement between the two solutions. It is also apparent that the
linear partitioning relationship alone is insufficient to characterize the effluent history curve.

The Freundlich relationship is used with the modified Kool model in the same manner as it is used in the analytical apparent partitioning model presented by Wise et al. The difference is that the numerical solution allows dispersivity to be included in the transport equation. The apparent nonlinear partitioning is most likely the result of mass transfer limited sites. Figure 3.19 demonstrates the capability of the modified Kool model to fit experimental data when using the Freundlich relationship.

![Graph showing model parameters and experimental data](image)

Figure 3.19  Modified Kool model with a Freundlich apparent partitioning relationship for the dissolution of toluene.

It is apparent that the Freundlich relationship can fit the earlier time data reasonably well but fails to fit the tail of the
effluent history curve. The failure to fit the tail of the curve is due to the exclusion of mass transfer limitations and the limited flexibility of the Freundlich relationship.

The Langmuir relationship is used with the modified Kool model in the same manner as the Freundlich partitioning relationship. Similarly, the apparent nonlinear partitioning is most likely the result of mass transfer limited sites. Figure 3.20 demonstrates the capability of the modified Kool model to fit experimental data when using the Langmuir relationship.

![Graph showing model parameters and experimental data fitting](image)

**Figure 3.20** Modified Kool model with a Langmuir apparent partitioning relationship for the dissolution of toluene.

It is apparent from figure 3.20 that the Langmuir relationship is also incapable of fully characterizing the effluent history curve.
This should be expected of the Langmuir relationship since it will approach a linear relationship at low aqueous phase concentrations.

A weighting function was applied to the square of the residuals with each of the three partitioning relationships. The weighting function was defined as the inverse of the observed concentration squared. However, the weighting procedure actually resulted in worse fits to the data due to the inflexibility of the three relationships.

Modified Kool Model as a Submodel

The modified Kool model is limited in its usefulness as a submodel to a horizontal transport model. However, one advantage it does possess is that it can easily be modified to include first-order decay of a solute.

The primary disadvantage of the modified Kool model is that only the linear relationship could be employed with independently determined parameters, and this would only be adequate where mass transfer limitations were negligible. The disadvantage of the Freundlich relationship is that it would require calibration to site specific soil column data or a more sophisticated model. In this case, the model presented by Wise et al. is computationally more efficient.
Chapter 4

An Investigation of Decoupling the Transport Equations for a Multicomponent Oil

Several investigators have presented models which couple transport equations for each component of a multicomponent non-aqueous phase liquid. The model presented by Borden, et al. (1989) is an example of this approach applied to the dissolution of BTEX components from a multicomponent residual oil. The equations are coupled in order to develop a more accurate description of the oil/water partitioning through time. The variability is primarily a result of the selective removal of the more soluble components of a residual oil. Unfortunately coupled equations require a numerical modeling approach which can be computationally expensive, particularly when mass transfer limitations are considered. Borden reported computer run times of 1000 minutes on a MicroVax II for a coupled mass transfer limited model (Borden, et al., Submitted 1990). The investigation presented here was initiated in an attempt to determine if and when coupling of the transport equations become necessary for adequately describing the dissolution of a single component from a multicomponent oil.

Problem Development

The equilibrium partitioning of an individual residual oil component, such as m+p-xylene, between a multicomponent residual
oil and an infiltrating water is not constant through time. The slight variability is a result of the functional relationship between the equilibrium aqueous phase concentration and the mole fraction of an individual component. An expression to describe the equilibrium partitioning can be derived by equating the activities in the water and oil phases (Stumm, et al., 1981). This results in an expression which is commonly used to estimate the equilibrium aqueous phase concentration of a hydrocarbon component,

$$C_i(H_2O) = C_{si(H_2O)} \chi_i(oil)$$  \hspace{1cm} (4.1)

Where \(C_i(H_2O)\) is the concentration of the component \(i\) in the water phase (mole/L\(^3\)), \(C_{si(H_2O)}\) is the saturation concentration of the pure component \(i\) in the water phase (mole/L\(^3\)), and \(\chi_i(oil)\) is the mole fraction of the component \(i\) in the oil phase. This expression assumes that the standard state activity coefficients are equal to unity.

Equation (4.1) can be redefined upon substitution for \(\chi_i(oil)\). The resulting expression is,

$$C_i(H_2O) = C_{si(H_2O)} \frac{n_i(oil)}{\Sigma n_j(oil)}$$  \hspace{1cm} (4.2)

Where \(n_i(oil)\) is the number of moles of the component \(i\) in the oil phase (mole/L\(^3\)), and \(\Sigma n_j(oil)\) is the total number of moles for all the components in the oil phase (mole/L\(^3\)).

It is apparent from equation (4.2) that the aqueous phase equilibrium concentration \(C_i(H_2O)\) will increase as \(n_i(oil)\) for a less
soluble component remains constant while the $\Sigma n_j(oil)$ decreases as the more soluble components, such as benzene, are selectively removed from the residual oil. This is the mechanism which results in a partitioning relationship which is not exactly constant through time.

The development of the problem is completed with a description of the assumptions made when transport equations are coupled and decoupled for multicomponent residual oils. When transport equations are coupled, the $\Sigma n_j(oil)$ is redetermined at every time step within a simulation. When transport equations are decoupled, the $\Sigma n_j(oil)$ is assumed constant throughout a simulation. The significance between the two assumptions is primarily dependent on the magnitude of the change in the $\Sigma n_j(oil)$. Therefore, it is expected that the less soluble components will be effected to a greater extent than the more soluble components.

Development of the Multicell Model

A simple model was developed to investigate the significance of coupling the transport equations. Conceptually, it is similar to the numerical model presented by Rixey, et al. (1990) to evaluate experimental data collected from soil flushing. The Multicell model was developed using the simulation software package STELLA (Richmond, et al., 1987). STELLA was used because it provides an object oriented user interface which greatly facilitates the building of
simple models. Figure 4.1 is a STELLA diagram for one subcell of the Multicell model.

![Diagram representation of a subcell of the Multicell model.](image)

Figure 4.1  Diagram representation of a subcell of the Multicell model.

The object labeled "ci" is called an accumulator. The accumulator represents the mass of a component, i, contained in one arbitrary unit volume of residual oil. The arbitrary unit volume would be the minimum volume required to reach equilibrium with the advecting water at a constant flux. The object labeled "cwi" is a calculation cell. The calculation performed here is to determine the equilibrium partitioning of a component between the residual oil and the aqueous phase. The object labeled "didt" is called a flow controller. Its function is to remove mass from the accumulator. The cloud represents a flow which is discarded. In equation form, the subcell can be described as follows:

\[ C_{wi} = C_{si(H2O)} x_i(oil) \]  \hspace{1cm} (4.3)

\[ \text{didt} = \left( C_{wi(cell \ n)} - C_{wi(cell \ n-1)} \right) \frac{\theta_w}{\theta_o} \]  \hspace{1cm} (4.4)

and \[ C_i = C_i + dt \times (-\text{didt}) \]  \hspace{1cm} (4.5)
Where $C$ is concentration (mole/L$^3$), $dt$ is the time step ($T$), $x_{i\text{(oil)}}$ is the mole fraction of the component $i$ in the oil phase, and $\theta_w$ and $\theta_o$ are the bulk water and oil contents, respectively.

The simulation algorithm represented by equation (4.5) is the Euler's method; a 4th-order Runge-Kutta method is also available with STELLA. The results presented here were generated using the 4th-order Runge-Kutta method.

The processes of dispersion and mass transfer limited kinetics are neglected in the Multicell model. However, this should not present a problem since the intent of the model is to investigate fundamental relationships between coupled and decoupled transport equations.

The model was designed to use the data reported by Borden. Therefore, the model contains four subcells, one for each of the predominant aromatic components, benzene, toluene, and m+p-xylene, and one for the remaining components (primarily the aliphatic fraction.) The four subcells together represent the residual oil. The model represents coupled transport when the subcells are linked together, and decoupled transport when the subcells are not linked. Furthermore, to complete the model, there are twenty sets of subcells, each representing the minimum volume necessary to reach equilibrium at a constant flux.
The execution of the model is very simple. At the dimensionless time $\tau = 0$, each of the accumulators are initialized with a mass equal to the initial concentration of the residual oil. At each time step, the equilibrium aqueous phase concentration is determined for each subcell. Then the flow controller removes mass from the accumulator if $C_{wi}$ at cell $n$ is greater than $C_{wi}$ at cell $n-1$; likewise, the flow controller adds mass if $C_{wi}$ at cell $n$ is less than $C_{wi}$ at cell $n-1$. The process is continued for whatever number of time steps is necessary to deplete the accumulators.

**Results**

The results for coupled equations is presented first. Figure 4.2 shows the normalized aqueous phase concentration versus time at the last cell in the model. There is a noticeable increase in the aqueous phase concentration of about 10% for the component m+p-xylene. It is interesting to note that the increase in concentration is most pronounced when the concentration of the more soluble component toluene has begun to decline. The initial mole fraction of the different components are shown in table 4.1.

It is not surprising that little effect was noticed when only the benzene fraction was depleted since the benzene fraction is relatively small. The phenomenon depicted in figure 4.2 has also been observed in soil column venting experiments with gasoline-range hydrocarbon mixtures (personal communication with P. Johnson, Shell Development Company.)
**Table 4.1** Properties of the residual oil used in the Multicell model.

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction</th>
<th>Pure Phase Solubility (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
<td>0.015</td>
<td>1780</td>
</tr>
<tr>
<td>toluene</td>
<td>0.072</td>
<td>515</td>
</tr>
<tr>
<td>m+p-xylene</td>
<td>0.049</td>
<td>198</td>
</tr>
<tr>
<td>aliphatics</td>
<td>0.864</td>
<td>9.5 (average)</td>
</tr>
</tbody>
</table>

**Figure 4.2** Aqueous concentration at cell no. 20. The dissolution of a residual oil with a coupled partitioning relationship.

A plot of aqueous phase concentration versus distance at time $\tau = 1280$ pore volumes is shown in figure 4.3 for the component m+p-xylene. It is apparent from figure 4.3, that mass is transferred from the aqueous phase back to the residual oil as the equilibrium
solubility of m+p-xylene approaches its initial value downstream of the retreating concentration fronts of the more soluble components.

![Graph showing aqueous concentration of m+p-xylene vs distance](image)

Figure 4.3  Aqueous concentration of m+p-xylene vs distance. The dissolution of a residual oil with a coupled partitioning relationship.

It would be particularly interesting to be able to predict the maximum increase in the aqueous phase concentration that might be expected for a particular component of a multicomponent residual oil. Unfortunately, it appears that the maximum concentration is also scale dependent, and that each component, with the exception of the most soluble component, approaches a significantly higher aqueous phase concentration with increased distance into the residual oil zone. The maximum concentration appears to be limited only by the initial fraction of less soluble components and the maximum residual oil saturation. The least soluble component, will approach its pure
phase aqueous concentration as the other fractions are depleted. The point is that the maximum increase in the aqueous phase concentration is dependent on the oil mixture and the scale of the system. Figure 4.4 depicts the increase in aqueous concentration for m+p-xylene as a function of time and location. Note that the wave increases in height and width as it progresses downgradient.

Figure 4.4 Aqueous concentration of m+p-xylene vs time. The dissolution of a residual oil with a coupled partitioning relationship.

It is also interesting to view the partitioning relationship through time. Figure 4.5 shows the partitioning between the oil and water phases for the component m+p-xylene at cell number 1. It is interesting to note that the time-varient partitioning changes in the opposite direction as that assumed by the apparent partitioning model. It is also interesting that the time-varient partitioning is also scale dependent. This is apparent by figure 4.6 which shows the
partitioning between the oil and water phases for the component m+p-xylene at cell number 20. At cell number 20, the concentration increases initially in both the oil and water phases.

Figure 4.5  Time-variant partitioning of m+p-xylene at cell number 1. The dissolution of a residual oil with a coupled partitioning relationship.
Figure 4.6 Time-variant partitioning of m+p-xylene at cell number 20. The dissolution of a residual oil with a coupled partitioning relationship.

Figure 4.7 is shown for comparison. This figure shows the results for decoupled transport equations. In this case, the sum of the concentrations for the residual oil components is assumed to be unchanged by the removal of the more soluble components. This is also the assumption made for each of the transport models evaluated in Chapter 3 of this work. It is impossible to determine precisely how inaccurate the decoupled transport assumption may be for the experimental data presented by Borden due to the amount of scatter associated with the measured aqueous phase concentrations.
Figure 4.7 Aqueous concentration at cell no. 20. The dissolution of a residual oil with a decoupled partitioning relationship.

**Discussion**

The intent of the Multicell model investigation was to determine if and when coupling of the transport equations becomes necessary for adequately describing the dissolution of a component from a multicomponent oil. The problem has been determined to be a function of the hydrocarbon mixture, the scale of the system, and the kinetics of the system. The kinetics of the system is described in the Multicell model as the minimum pore volume necessary for a component to reach an equilibrium concentration with the advecting water phase. This appears to be the limiting information for a direct solution to the problem. However, two observations can be made. First, the transport of the most soluble component of the residual oil
will be completely unaffected by a decoupled solution. Second, the
data reported by Borden, et al. (1989) and Rixey, et al. (1990) for
gasoline-range hydrocarbon mixtures do not appear to exhibit any
significant increase in aqueous phase concentration of the less
soluble BTEX components. Rixey, et al. (1990) also reported
experimental data for a prepared hydrocarbon mixture which
contained a 20% fraction of benzene. The prepared mixture showed
only a slight increase in the aqueous phase concentration of the less
soluble components.
Chapter 5

Modification of BIOPLUME II

The apparent partitioning model presented by Wise et al. has been linked to the 2-D horizontal contaminant transport model BIOPLUME II v1.0 (Rifai, et al., 1987). The intent of the modification was to develop a model which could simulate the continuous time-variant source of contamination due to vertical infiltration of water past a residual oil and the subsequent horizontal transport of the contaminants. The capability of the modified model is demonstrated with an application to a hypothetical site. Furthermore, the apparent partitioning function is compared to other methods which are available for describing the residual oil source effluent concentration. Finally, the limitations of the model and possible improvements to the model are discussed.

Link to BIOPLUME II

The link to BIOPLUME II was accomplished primarily by the addition of a subroutine which modifies a contaminant source concentration variable at each time step of the transport model. This variable existed in the original BIOPLUME code as a constant contaminant source concentration. Figure 5.1 demonstrates how the modified model approximates the residual oil source effluent curve. The approximation shown in figure 5.1 was made utilizing the fitted
parameters obtained from the Borden data for the component toluene.

![Graph](image)

**Figure 5.1** BIOPLUME II approximation for the dissolution of toluene from a residual oil, tolerance criteria (DLTC) = 0.40.

The use of an existing variable minimized the required modification to the existing code. However, one modification to the existing code was made to include a tolerance criteria for the minimum number of time steps required to characterize the effluent concentration history curve. The variable name for the tolerance criteria is DLTC. The value of DLTC is set by the model user. A smaller value for DLTC results in a closer approximation of the effluent history curve. However, it also results in a greater model execution time. **Figure 5.2** shows the result of a smaller tolerance criteria. The input parameters associated with figure 5.1 and figure 5.2 are identical with the exception of the tolerance criteria.
There were other less significant modifications made to the BIOPLUME II v1.0 code. A detailed description of these modifications and a copy of the modified code is included in Appendix D.

![Graph](image)

Figure 5.2  BIOPLUME II approximation for the dissolution of toluene from a residual oil, tolerance criteria (DLTC) = 0.05.

**Demonstration of Applicability**

The capability of the modified code is demonstrated with an application to a hypothetical site and a comparison to existing alternatives for simulating a residual oil source of contamination.

**Application to a Hypothetical Site**

The hypothetical site was designed to mimic a situation similar the that depicted in figure 1.1, where a residual oil zone is located
directly above the water table of an unconfined aquifer. The horizontal flow and transport characteristics for the hypothetical site can be further described by the following model characteristics:

1. Grid dimension -15 by 20 (750 ft by 1000 ft)
2. Cell size - 50 ft on each side (300 cells)
3. Hydraulic Conductivity = 0.0001 ft/s (constant over grid)
4. Aquifer thickness = 25 ft
5. Aquifer porosity = 0.30
6. Hydraulic gradient = 0.003 ft/ft, this results in an average pore water velocity of 0.09 ft/day
7. Biodegradation is assumed not to occur.

The residual oil zone was assumed to be of constant thickness and cover the area of one cell. The vertical flow and transport characteristics for the residual oil zone can be further described by the following model characteristics:

1. An infiltration rate of 9.0e-7 ft/s is assumed (equivalent to infiltrating 12 in/yr of rainfall)
2. A multicomponent oil identical to that reported for Borden's experiment is assumed. The fitted parameters obtained for the Borden data are used (Table 3.2.)
3. The mass transfer limited characteristics associated with the higher pore water velocities of the Borden experiment were assumed unchanged. This was done for illustrative purposes even though it is an unlikely situation.
Figure 5.3 shows the modified model's approximation to the effluent history curve for the residual oil zone. The effluent curve represents the aqueous concentration leaving the bottom of the residual oil zone and entering the unconfined aquifer at the water table. The effluent concentration history does not actually end abruptly at 740 pore volumes as shown in figure 5.3. The curve was cut off at 740 pore volumes in order to illustrate the character of the earlier time dissolution of the residual oil components. Actually, the curve would continue at the equilibrium concentration of the aliphatic fraction for more than 12000 pore volumes.

![Apparent Partitioning Model](image)

Figure 5.3 Effluent history approximation for the dissolution of a multicomponent residual oil.

The model is first demonstrated with a comparison of two sources, each with a different residual oil zone thickness. The
aqueous concentration plume map is shown in figure 5.4. The source on the left side of the plume map has an assumed residual oil zone thickness of 0.25 feet and the source on the right, 0.125 feet. Note that in each of the plume maps presented, \( \zeta \) refers to the residual oil zone thickness. Several observations can be made from figure 5.4. First, the mass of contaminant associated with the plume on the left is twice the mass associated with the plume on the right. This is a direct result of the assumed residual oil zone thickness. The effluent history curve shown in figure 5.3 is independent of zone thickness and therefore is representative of both sources. At \( \Delta t = 20 \) years the amount of water flushed by each residual oil zone is 740 and 1480 pore volumes for the source with \( \zeta \) equal 0.25 and 0.125, respectively. Second, the maximum aqueous concentration appears to travel at the same velocity for both plumes as it is expected. Third, the aqueous concentration near the source at \( \Delta t = 20 \) years is identical for both plumes due to the aliphatic fraction that remains at both sources. However, the aliphatic fraction for both residual oil zones will eventually be depleted, and furthermore, the source with half the thickness will deplete in half the time of the other source.
Figure 5.4 Dissolved plume concentration at $\Delta t = 20$ years for a residual oil zone thickness of 0.25 ft compared to 0.125 ft.
Comparison to a Constant Source Approximation

The existing version of BIOPLUME II and several other transport models allow for the continuous input of a contaminant source at a constant concentration. Therefore, the modified version of BIOPLUME II is compared to the results produced by a constant source in order to demonstrate the improvement made by the more descriptive source input. The comparison is shown in figure 5.5. The plume shown on the left is the same as that presented in the previous figure for $\xi = 0.25$ feet. The plume on the right represents a mass of contaminant which has been released from the residual source at a constant concentration of 27.0 mg/l. Both plumes represent an identical mass of contaminant. The most significant observation to be made from figure 5.5 is that a constant source results in an inaccurate distribution of mass in the dissolved plume.

Several transport models allow for the step input of a contaminant source of constant concentration which is variable with each time step. Certainly the effluent history curve for a residual oil source could be adequately approximated given a sufficient number of time steps. Furthermore, the resulting plume generated from a step input would most likely compare well with that generated by the modified BIOPLUME II model, particularly for situations with minimum mass transfer effects. Although this approach may be effective, it would be awkward to utilize in a modeling study which would require the evaluation of variable infiltration rates.
Figure 5.5  Dissolved plume concentration at $\Delta t = 20$ years for a variable source compared to a constant source.
Comparison to an Exponentially Declining Source Approximation

Transport models are available which allow for the input of an exponentially declining contaminant source. Therefore, the results of the time-variant version of BIOPLUME II are compared to the results produced for an exponentially declining contaminant source. The modified version of BIOPLUME II was modified further in order to produce the exponentially declining contaminant source. The modification replaced the apparent partitioning time-variant source function with one for exponential decline. The resulting effluent history curve is shown in figure 5.6. The resulting contaminant plume is shown in figure 5.7. The plume shown on the left is the same as that presented in figure 5.4 for $\zeta = 0.25$ feet. The plume on the right represents a mass of contaminant which has been released at an exponentially declining rate. Both plumes represent an identical mass of contaminant. It is apparent that the exponential function does a relatively good job of producing a comparable dissolved plume. However, it is also apparent that the exponential function is beginning to fail near the source as the exponential function continues to rapidly approach lower effluent concentrations. This could be a problem if modeling were required at times much greater than that required to flush the more soluble components, that is, when the effluent curve flattens out. Furthermore, using the exponential function will require a complete description of the
effluent history curve and a calculated decline constant calibrated for the expected duration of the simulation.

Figure 5.6  An exponential decline approximation for the dissolution of a multicomponent residual oil.
Figure 5.7  Dissolved plume concentration at $\Delta t = 20$ years for a variable source compared to a constant source.
Discussion of Limitations

The limitations of the modified model are primarily a function of the limitations imposed by the apparent partitioning model and the limitations inherent in determining the necessary input parameters to describe the residual oil source system. The most significant limitations are listed below.

Limitations imposed by the apparent partitioning model:

1. Decoupled transport equations
2. No provision for biodegradation
3. Vertical infiltration limited to constant flux
4. Assumes 0% vapor saturation, therefore, no volatilization
5. The apparent partitioning model must be calibrated to soil column data or a more sophisticated model.

Limitations inherent in determining the necessary input parameters:

6. The pore water velocity due to infiltration is variable and difficult to accurately measure.
7. The composition and mass of the residual oil zone can be difficult to quantify.

The simplifying assumption is made that the aqueous solubility of a single component of a multicomponent oil is independent of the other components. This limitation is required for decoupled transport equations. However, the effect appears to be minimal for
systems with a residual oil source composed of gasoline range hydrocarbons. The minimal effect is apparent from the experimental data presented by Borden, et al. (1989) and Rixey, et al. (1990). It also appears that this limitation is minimized for systems with a residual oil source which is located above the water table. The effect is minimized because the redistribution of mass of the less soluble components is a function of the scale of the problem, and the scale is typically small for systems limited to vertical infiltration.

One of the most significant limitations of the model is that there is no provision to account for first order decay of the solute in the residual oil source zone. However, this limitation equally applies to most other available transport models.

Limiting vertical infiltration to a constant flux condition can be significant when the actual flux is highly variable. The constant flux limitation will always be a problem for analytical solutions.

The apparent partitioning model is not appropriate for predicting the dissolution of a component from a multicomponent residual oil source without prior calibration. However, the calibration can be made to either soil column data or a more sophisticated model.

The limitations inherent in determining the necessary input parameters are perhaps the most significant limitations of any transport model.
Foreseeable Improvements

Foreseeable improvements which can be made to modeling the dissolution of contaminants from a residual oil source and the subsequent horizontal transport should focus on minimizing the effects of the previously defined limitations.

One of the simplest improvements would be the integration of the two-site model with BIOPLUME II. This would produce a model with a much more appropriate predictive capability. Furthermore, an analytic solution which incorporates both two-site dissolution and a first-order decay would be a considerable improvement.

Another improvement, which is related to the incorporation of the two-site model, would be a better understanding of the relationship between the measured values and the fitted values for $\alpha$ and $\beta$, the mass transfer coefficient and the fraction of equilibrium controlled sites, respectively. Also related to the incorporation of the two-site model, would be the incorporation of a stochastic estimation procedure which could simulate the variability of required input parameters for the model for a specific area.

Finally, a significant improvement would be an extension of the model to the case of a residual oil source which is located within the saturated zone.
Chapter 6

Conclusions

Only recently have researchers begun to focus on modeling the dissolution of residual non-aqueous phase liquids in the subsurface. This is evident by the recent increase in published research on the topic in the last five years. The impetus for the research arises from a need to clean up numerous contaminated waste sites which contain residual oils and the high cost associated with the cleanup. Furthermore, it appears that researchers will continue to focus on the dissolution of residual oils as there are numerous unanswered questions regarding this topic. The research presented here has been an attempt to answer some of these questions.

The first objective of the research presented here was to evaluate contaminant transport models which might be applicable to modeling the dissolution of a residual oil source due to vertical infiltration of water. Three models were selected and evaluated. The first model evaluated was a modified version of the two-site adsorption model presented by Parker, et al. (1984). The second model evaluated was the apparent partitioning model presented by Wise, et al. (To Be Submitted 1991). The third model evaluated was a modified version of the adsorption model presented by Kool, et al. (1989). A conclusion which can be drawn from this evaluation is that each of the three models have limited applicability, but the two-
site model is most likely the best suited to be used as a submodel to a horizontal transport model.

The second objective of this research was to incorporate an appropriate contaminant transport model for the dissolution of a residual oil source into a horizontal transport model. Therefore the apparent partitioning model has been linked to the two-dimensional contaminant transport model BIOPLUME II. The result is a model capable of characterizing the continuous time-variant contaminant source due to vertical infiltration of water past a residual oil and the subsequent horizontal transport of the contaminant; this capability was previously unavailable in contaminant transport models.

The third objective was to demonstrate the capability and the limitations of the modified transport model. The capability of the modified model is demonstrated with an application to a hypothetical site. Furthermore, a comparison is made between the modified model and existing alternatives for modeling aquifer contamination from a residual oil source. The result is that the modified model offers a significant improvement in the source term characterization. The primary limitations of the model include the limitations inherent in determining the necessary input parameters and the limitations associated with the apparent partitioning model.

A secondary objective was identified as a result of the evaluation of contaminant transport models for the dissolution of a residual oil source. This objective was to investigate the effect of
decoupling the transport equations for a multicomponent oil. Two conclusions were derived from this investigation. First, the effect of decoupling the transport equations is a function of both the composition of the residual oil and the scale of the system to be considered. Second, the effect of decoupling the transport equations is most likely insignificant for systems of gasoline range hydrocarbons which are subject only to vertical infiltration of water.
Appendix A

Two-Site Model

The two-site model code developed by Parker, et al. (1984) for evaluating break through curves has been slightly modified, primarily for more convenient use.

Parker Code Modifications

The original Parker code, "CXTFIT", was written in FORTRAN. The code has been modified and compiled for execution on a Mac II. Modifications were made only to the main program. The modifications are as follows:

1. The original plot file option was disabled and a new option was added. The new plot file option writes the pore volumes flushed and the calculated concentration for each observation time. A tab delimiter is written between the two output variables which allows the plot file to easily be imported into a plotting application, e.g., CricketGraph or DeltaGraph.

2. Unit numbers 5 and 6 were changed to 15 and 16, respectively.

3. An option was added to weight the sum of the squared residuals by $1/c^2$, with $c$ being the observed aqueous concentration.
4. Tab delimiters were included in the write statements of the output file.

**Use of the Modified Two-Site Model Code**

The use of the modified model is identical to that of the original model with the exception that a weighting function must be specified following entry of the input data set filename. The necessary input parameters are defined in Chapter 3 of this work.
Modified Main Program Listing

The modified main program code listing is included here. Code modifications are preceded and followed by the comment line CGCR. The subroutines and functions which were not modified are not included here. These can be found in the work presented by Parker, et al. (1984).

PROGRAM RSCXT

*****************************************************************
* CXTFIT: NON-LINEAR LEAST-SQUARES ANALYSIS OF C(X,T) DATA        *
* FOR ONE-DIMENSIONAL DETERMINISTIC OR STOCHASTIC SOLUTE          *
* TRANSPORT WITH DETECTION IN RESIDENT OR FLUX MODES              *
*                                                               *
*                                                               *
* SEE: J. C. PARKER AND M. TH. VAN GENUCHTEN. 1984.              *
* "DETERMINING TRANSPORT PARAMETERS FROM LABORATORY AND          *
* FIELD TRACER EXPERIMENTS" VA. AG. EXP. STA. BULL. 84-3.        *
*                                                               *
* FORTRAN 77 VERSION 2.1 SEPTEMBER 1985                         *
* NOTE: METACOMMANDS FOR MS-FORTRAN/3.3                         *
* V. 2.2 MODIFIED FOR FPLOT OUTPUT MAR86                         *
*                                                               *
* MODIFIED BY GC ROBINSON, 3/17/91                              *
*                                                               *
******************************************************************

IMPLICIT REAL*8 (A-H,O-Z)
INTEGER FLAG7, IWF
CHARACTER*15 FILENAME, XIABEL
DIMENSION C(90),F(90),R(90),DELE(90,7),B(14),E(7),TH(14),P(7),
1PHI(7),Q(7),LSORT(90),TB(14),A(7,7),BI(14),TITLE(20),D(7,7),
2BMAX(7),BMIN(7),P0RV(90)
COMMON/MODAT1/X(90),T(90),INDEX(7),NOB,NREDU,NVAR
COMMON/MODAT2/CT,C0,DM1,DM2,DM3,DM4,DM5,DM6,DM7,DM8,DM9,DM10,
1DM11,DM12,MODE,MODT
COMMON/MODAT3/TPULSE(11),PULSE(11),CITEMP,NPULSE
DATA STOPCR/0.0005/
DATA MAXTRY/50/
FLAG7 = 1
C
C INITIALIZE UNITS 15 AND 16
WRITE(*, 2001)
READ(*, 2003) FILENAME
IF(FILENAME.EQ. ' ')FILENAME='CXTFIT.DAT'
OPEN(15, FILE = FILENAME, STATUS = 'OLD')

C
CGCR
WRITE(*,2006)
READ(*,2007) IWF
IF (IWF.EQ.2) GOTO 1
IWF=1
CGCR

C

1 WRITE(*, 2002)
READ(*, 2003) FILENAME
IF(FILENAME.EQ. ' ')FILENAME='CXTFIT.OUT'
OPEN(16, FILE = FILENAME, STATUS = 'NEW')

C
C
CGCR
WRITE(*, 2002)
READ(*, 2003) FILENAME
IF(FILENAME.EQ. ' ')FILENAME='CXTFIT.GRF'
OPEN(17, FILE = FILENAME, STATUS = 'NEW')

CGCR
C
C
C
C
C ---- READ NUMBER OF CASES -----
READ(15,1006) NC
DO 150 NCASE=1,NC
C
C
C ---- READ INPUT PARAMETERS -----
READ(15,1006) MODE, NDATA, NREDU, MIT, NOB, NSKIP, NPRNT
C
C UNIT 7 DECLARATION
IF (NPRNT.GE.2) THEN
  IF(FLAG7.EQ.0) THEN
    WRITE(*,2004)
    READ(*,2003) FILENAME
    IF(FILENAME.EQ. ' ')FILENAME='CXTFIT.PLT'

    OPEN(UNIT = 7, FILE = FILENAME, STATUS = 'NEW')
    FLAG7 = 1
    IF (NPRNT.EQ.2) THEN
      XLABEL = 'DISTANCE'
    ELSE
      XLABEL = 'TIME'
    ENDIF
  IF(NPRNT.NE.4) WRITE(7, 2003) XLABEL
  ELSE
    IF(NPRNT.NE.4) NPRNT = 0
  ENDIF
ENDIF
C
IF(NSKIP.NE.0) GO TO 2
WRITE(16,1000)
101

IF(MIT.NE.0) WRITE(16,1035)
WRITE(16,1036)
M=(MODE-1)/2
IF(M.EQ.0) WRITE(16,1021)
IF(M.EQ.1) WRITE(16,1022)
IF(M.EQ.2) WRITE(16,1023)
IF(M.EQ.3) WRITE(16,1039)
N=MODE-2*M
IF(N.EQ.1) WRITE(16,1024)
IF(N.EQ.2) WRITE(16,1025)
IF(NREDU.EQ.1) WRITE(16,1037)
IF(NREDU.EQ.2) WRITE(16,1040)
WRITE(16,1036)

2 NVAR=6
IF(MODE.GE.5) NVAR=7
NU1=NVAR+1
NU2=2*NVAR
DO 4 I=1,2
READ(15,1001) TITLE
4 IF(NSKIP.EQ.0) WRITE(16,1002) TITLE
   IF(NSKIP.EQ.0) WRITE(16,1003)

C
C       READ COEFFICIENTS NAMES -------
READ(15,1004) (BI(I),I=1,NU2)
C
C       READ INITIAL ESTIMATES -------
READ(15,1005) (B(I),I=NU1,NU2)
C
C       READ INDICES -------
READ(15,1044) ILMT, (INDEX(I),I=1,NVAR)
C
C       READ CONSTRAINTS ON PARAMETER VALUES -------
IF(ILMT.EQ.0) GO TO 5
READ(15,1005) (BMIN(I),I=1,NVAR)
READ(15,1005) (BMAX(I),I=1,NVAR)
5 IF((MODE.LT.3).OR.(MODE.GT.4)) GO TO 6
   IF((BMAX(5).EQ.0).OR.(BMAX(5).GT.1.)) BMAX(5)=1.0
C
C       READ INITIAL AND INLET CONCENTRATIONS -------
6 READ(15,1045) CI,C0,NPULSE
   IF(NPULSE.LT.1) NPULSE=1
   IF(NSKIP.NE.0) GO TO 8
   WRITE(16,1007)
   DO 7 I=1,NVAR
      IF((NPULSE.GT.1).AND.(I.EQ.4)) GO TO 7
      J=2*I-1
   WRITE(16,1008) BI(J),BI(J+1),B(I+NVAR)
   7 CONTINUE

8 IF(NSKIP.EQ.0) WRITE(16,1026) CI
   IF((NSKIP.EQ.0).AND.((NPULSE.EQ.1).OR.(MODE.GE.7)))
   1 WRITE(16,1049) C0
   IF(NPULSE.EQ.1)GO TO 11
   IF(NSKIP.NE.0) GO TO 9
   IF(MODE.LE.6) WRITE(16,1046)
   IF(MODE.GT.6) WRITE(16,1047)
9 INDEX(4)=0
DO 10 I=1,NPULSE
    NUM=0
    IF(MODE.LT.7) NUM=1
    READ(15,1005) TPULSE(I+NUM), PULSE(I+1)
    IF((NSKIP.EQ.0).AND.(MODE.LT.7))
        1 WRITE(16,1048) I, TPULSE(I), TPULSE(I+1), PULSE(I+1)
    10 IF((NSKIP.EQ.0).AND.(MODE.GE.7))
        1 WRITE(16,1048) I, TPULSE(I), PULSE(I+1)
    IF(NDATA.NE.1) GO TO 13

C C ----- READ AND WRITE EXPERIMENTAL DATA -----  
X1=0.0
DO 12 I=1,NOB
    READ(15,1005) C(I), X(I), T(I)
    12 X1=DMAX1(X1, X(I))
IF(NSKIP.NE.0) GO TO 150
    IF(NREDU.NE.2) GO TO 17
    INDEX(1)=0
    INDEX(I)=0
    17 IF(MIT.EQ.0) GO TO 28
       IF(NPRNT.NE.1) GO TO 25
       WRITE(16,1009)
       DO 24 I=1,NOB
       WRITE(16,1010) I, C(I), X(I), T(I)
    24 CONTINUE

C C ----- CHECK FOR INPUT ERROR -----  
25 NZC=0
26 NFC=0
DO 27 I=1,NVAR
    IF((B(I+NVAR).EQ.0.0).AND.(I.LE.3)) GO TO 129
    IF((B(I+NVAR).EQ.0.0).AND.(INDEX(I).EQ.1)) GO TO 130
    IF((I.EQ.4).OR.(MODE.GE.5)) GO TO 27
    IF(INDEX(I).EQ.1) NFC=NFC+1
    IF(B(I+NVAR).NE.0.0) NZC=NZC+1
    27 CONTINUE
    IF(MODE.GE.5) GO TO 28
    IF(NZC.LE.NFC) GO TO 120

C C ----- REARRANGE VARIABLE ARRAYS -----  
28 NP=0
    DO 30 I=NU1,NU2
        TB(I)=B(I)
        IF(INDEX(I-NVAR).EQ.0) GO TO 30
        NP=NP+1
        K=2*NP-1
        J=2*(I-NVAR)-1
        BI(K)=BI(J)
        BI(K+1)=BI(J+1)
        B(NP)=B(I)
        TB(NP)=B(I)
        TH(NP)=B(NP)
        BMN(NP)=BMN(I-NVAR)
        BMX(NP)=BMX(I-NVAR)
    30 TH(I)=B(I)

C C ----------
GA=0.02
NIT=0
NE2=2*NP
CALL MODEL(TH,F)
IF (NIT.EQ.0) GO TO 140
SSQ=0.
DO 32 I=1,NP
   R(I)=C(I)*F(I)
C
CGCR
   IF (IWF.EQ.2) R(I)=R(I)/C(I)
C
CGCR
   32 SSQ=SSQ+R(I)*R(I)
   WRITE(16,1011) (BI(J),BI(J+1),J=1,NP2,2)
   WRITE(16,1012) NIT,SSQ,(B(I),I=1,NP)
C
C ------- BEGIN ITERATION -------
   34 NIT=NIT+1
   NTRIAL=0
   GA=0.1*GA
   DO 38 J=1,NP
      TEMP=TH(J)
      TH(J)=1.01*TH(J)
      Q(J)=0.
      CALL MODEL(TH,DELZ(1,J))
   DO 36 I=1,NP
   C
CGCR
   IF (IWF.EQ.1) DELZ(I,J)=DELZ(I,J)-F(I)
   IF (IWF.EQ.2) DELZ(I,J)=(DELZ(I,J)-F(I))/C(I)
CGCR
   C
   36 Q(J)=Q(J)+DELTZ(I,J)*R(I)
   Q(J)=100.*Q(J)/TH(J)
C
C ------- Q=XT*R (STEEPEST DESCENT) -------
   38 TH(J)=TEMP
   DO 44 I=1,NP
      DO 42 J=1,I
         SUM=0.
      DO 40 K=1,NP
         40 SUM=SUM+DELTZ(K,I)*DELTZ(K,J)
      D(I,J)=10000.*SUM/(TH(I)*TH(J))
   42 D(J,I)=D(I,J)
   E(I)=DSQRT(D(I,I))
   44 IF (E(I).EQ.0.) E(I)=1.D-30
   50 DO 52 I=1,NP
      DO 52 J=1,NP
      52 A(I,J)=D(I,J)/(E(I)*E(J))
C
C ------- A IS THE SCALED MOMENT MATRIX -------
   DO 54 I=1,NP
      P(I)=Q(I)/E(I)
      PHI(I)=P(I)
   54 A(I,I)=A(I,I)+GA
   CALL MATINV(A,NP,P)
C
C ------- P/E IS THE CORRECTION VECTOR -------
STEP=1.0

56 DO 58 I=1,NP
   TB(I)=P(I)*STEP/E(I)+TH(I)
   IF(BMIN(I).EQ.BMAX(I)) GO TO 58
   IF(TB(I).GT.BMAX(I)) TB(I)=BMAX(I)
   IF(TB(I).LT.BMIN(I)) TB(I)=BMIN(I)
   P(I)=(TB(I)-TH(I))*E(I)/STEP
58 CONTINUE

60 DO 62 I=1,NP
   IF(TH(I)*TB(I)) 66,66,62
62 CONTINUE

SUMB=0.0
CALL MODEL(TB,F)
DO 64 I=1,NB
   R(I)=C(I)-F(I)

CGCR
   IF (IWF.EQ.2) R(I)=R(I)/C(I)
CGCR

64 SUMB=SUMB+R(I)*R(I)
66 SUM1=0.0
   SUM2=0.0
   SUM3=0.0
   DO 68 I=1,NP
      SUM1=SUM1+P(I)*PHI(I)
      SUM2=SUM2+P(I)*P(I)
   68 SUM3=SUM3+PHI(I)*PHI(I)
   ARG=0.0
   IF(SUM2*SUM3.NE.0.0) ARG=SUM1/DSQRT(SUM2*SUM3)
   ARG1=0.0
   IF(NP.GT.1) ARG1=DSQRT(1.-ARG*ARG)
   ANGLE=57.29578*DATAN2(ARG1,ARG)

C

---------
   DO 72 I=1,NP
   IF(TH(I)*TB(I)) 74,74,72
72 CONTINUE
   NTRIAL=NTRIAL+1
   IF(NTRIAL.GT.MAXTRY) GO TO 95
   IF((SUMB-SSQ)/SSQ.LT.1.D-06) GO TO 80
74 IF(ANGLE-30.0) 76,76,78
76 STEP=0.5*STEP
   GO TO 56
78 GA=10.*GA
   GO TO 50

C

------ PRINT COEFFICIENTS AFTER EACH ITERATION ------

80 CONTINUE
   DO 82 I=1,NP
56 DO 58 I=1,NP
   TB(I)=P(I)*STEP/E(I)+TH(I)
   IF(BMIN(I).EQ.BMAX(I)) GO TO 58
   IF(TB(I).GT.BMAX(I)) TB(I)=BMAX(I)
   IF(TB(I).LT.BMIN(I)) TB(I)=BMIN(I)
   P(I)=(TB(I)-TH(I))*E(I)/STEP
58 CONTINUE

60 DO 62 I=1,NP
   IF(TH(I)*TB(I)) 66,66,62
62 CONTINUE

SUMB=0.0
CALL MODEL(TB,F)
DO 64 I=1,NB
   R(I)=C(I)-F(I)

CGCR
   IF (IWF.EQ.2) R(I)=R(I)/C(I)
CGCR

64 SUMB=SUMB+R(I)*R(I)
66 SUM1=0.0
   SUM2=0.0
   SUM3=0.0
   DO 68 I=1,NP
      SUM1=SUM1+P(I)*PHI(I)
      SUM2=SUM2+P(I)*P(I)
   68 SUM3=SUM3+PHI(I)*PHI(I)
   ARG=0.0
   IF(SUM2*SUM3.NE.0.0) ARG=SUM1/DSQRT(SUM2*SUM3)
   ARG1=0.0
   IF(NP.GT.1) ARG1=DSQRT(1.-ARG*ARG)
   ANGLE=57.29578*DATAN2(ARG1,ARG)

C

---------
   DO 72 I=1,NP
   IF(TH(I)*TB(I)) 74,74,72
72 CONTINUE
   NTRIAL=NTRIAL+1
   IF(NTRIAL.GT.MAXTRY) GO TO 95
   IF((SUMB-SSQ)/SSQ.LT.1.D-06) GO TO 80
74 IF(ANGLE-30.0) 76,76,78
76 STEP=0.5*STEP
   GO TO 56
78 GA=10.*GA
   GO TO 50

C

------ PRINT COEFFICIENTS AFTER EACH ITERATION ------

80 CONTINUE
   DO 82 I=1,NP
   TH(I)=TB(I)
   WRITE (16,1012) NIT,SUMB,(TH(I),I=1,NP)
   DO 86 I=1,NP
      IF(DABS(P(I)*STEP/E(I))/(1.0D-20+DABS(TH(I)))-STOPCR) 86,86,94
86 CONTINUE
   GO TO 96
94 SSQ=SUMB
   IF(NIT.LT.MIT) GO TO 34
IF(NIT.EQ.MIT) WRITE(16,1034) MIT
GO TO 96
95 WRITE(16,1038) MAXTRY
C
C ----- END OF ITERATION LOOP -----  
96 CONTINUE
CALL MATINV(D,NP,P)
C
C ----- WRITE CORRELATION MATRIX ----- 
98 DO 102 I=1,NP
98 E(I)=DSQRT(D(I,I))
98 IF(E(I).EQ.0.) E(I)=1.D-30
98 IF(NP.EQ.1) GO TO 104
98 WRITE(16,1013) (I,I=1,NP)
98 DO 102 I=1,NP
98 DO 100 J=1,I
100 A(J,I)=D(J,I)/(E(I)*E(J))
102 WRITE(16,1014) I,(A(J,I),J=1,I)
C
C ----- CALCULATE REGRESSION COEFFICIENT 
104 SUMC=0.0
104 SUMC2=0.0
104 DO 106 I=1,NOB
104 SUMC=SUMC+C(I)
106 SUMC2=SUMC2+C(I)*C(I)
106 RSQ=1.-(SUMB/(SUMC2-SUMC*SUMC/NOB))
106 WRITE(16,1041) RSQ
C
C ----- CALCULATE 95% CONFIDENCE INTERVAL ------
108 Z=1./FLOAT(NOBS-NOB)
108 SDEV=DSQRT(Z*SUMB)
108 TVAR=1.96+z*(2.7135+z*(3.187936+2.466666*z**2))
108 IF(NP.EQ.1) WRITE(16,1042)
108 IF(NP.GT.1) WRITE(16,1015)
108 DO 108 I=1,NP
108 SECOFSE=SEOF*SEOF
108 TVA=TH(I)/SECOFSE
108 TSEC=TVAR*SECOFSE
108 TMCOE=TH(I)-TSEC
108 TPCOE=TH(I)+TSEC
108 J=2*I-1
108 IF(NP.EQ.1) WRITE(16,1043) I,ICI(J),ICI(J+1),TH(I),SECOFSE,TMCOE,TPCOE
108 IF(NP.GT.1) WRITE(16,1016) I,ICI(J),ICI(J+1),TH(I),SECOFSE,TVA,TMCOE,TPCOE
108 CONTINUE
C
C ----- PREPARE FINAL OUTPUT ------ 
110 LSORT(I)=1
110 DO 115 J=2,NOB
110 TEMP=R(J)
110 K=J+1
110 DO 111 L=1,K
110 LL=LSORT(L)
110 IF(TEMP>R(LL)) 112,112,111
111 CONTINUE
LSORT(J)=J
GO TO 115
112  KK=J
113  KK=KK-1
    LSORT(KK+1)=LSORT(KK)
    IF(KK-L) 114,114,113
114  LSORT(L)=J
115  CONTINUE
    WRITE(16,1017)
    DO 116 I=1,N0B
CGCR
116  WRITE(16,1018) I,CHAR(9),X(I),CHAR(9),T(I),CHAR(9),C(I)
    1,CHAR(9),F(I),CHAR(9),R(I)
CGCR
      WRITE(16,1019)
      DO 117 I=1,N0B
CGCR
      J=LSORT(N0B+1-I)
117  WRITE(16,1018) J,CHAR(9),X(J),CHAR(9),T(J),CHAR(9),C(J)
    1,CHAR(9),F(J),CHAR(9),R(J)
C
      IF (MODE.EQ.3 .OR. MODE.EQ.4) THEN
    DO 210 I=1,N0B
      FORV(I) = B(7) * T(I) / X(I)
210  WRITE(17,1210)FORV(I),CHAR(9),F(I)
ENDIF
CGCR
C
      ----- OUTPUT FOR PLOTTER
      IF(NPRTN.LT.2)GO TO 150
    DO 118 I=1,N0B
      IF(NPRTN.EQ.4) WRITE(7,2005) C(I),X(I),T(I),I
      IF(NPRTN.EQ.3) WRITE(7,2000) T(I),C(I),I
118  IF(NPRTN.EQ.2) WRITE(7,2000) X(I),C(I),I
    DO 119 I=1,N0B
      IF(NPRTN.EQ.4) WRITE(7,2005) F(I),X(I),T(I),I
      IF(NPRTN.EQ.3) WRITE(7,2000) T(I),F(I),I
119  IF(NPRTN.EQ.2) WRITE(7,2000) X(I),F(I),I
2000  FORMAT(2F10.5,I5)
2005  FORMAT(3F10.5,I5)
C
      GO TO 150
120  WRITE(16,1028)
    DO 125 I=1,NVAR
      J=2*I-1
    IF(I.EQ.4) GO TO 125
    IF((INDEX(I).EQ.1).AND.(B(I+6).NE.0.0))
1  WRITE(16,1029)BI(J),BI(J+1)
125  CONTINUE
      GO TO 150
129  WRITE(16,1032)
      GO TO 150
130  WRITE(16,1031)
      GO TO 150
140  WRITE(16,1030)
    DO 145 I=1,N0B
------ OUTPUT FOR PLOTTER ------

IF (NPRINT.EQ.4) WRITE(7,2005) F(I),X(I),T(I),I
IF (NPRINT.EQ.3) WRITE(7,2000) T(I),F(I),I
IF (NPRINT.EQ.2) WRITE(7,2000) X(I),F(I),I

CGCR
145 WRITE(16,1033)I,CHAR(9),X(I),CHAR(9),T(I),CHAR(9),F(I)

IF (MODE.EQ.3 .OR. MODE.EQ.4) THEN
DO 220 I=1,NOB
   FORV(I) = B(7) * T(I) / X(I)
220 WRITE(17,1210)FORV(I),CHAR(9),F(I)
ENDIF

CGCR
150 CONTINUE

------ END OF PROBLEM ------

999 FORMAT(2F10.4,i5)
1000 FORMAT(//1X,82(1H*)/1X,1H*,80X,1H*/1X,1H*,10X,'ONE-DIMENSIONAL CO
   INVECTION-DISPERSION EQ. SOLUTION',20X,1H*)
1001 FORMAT(20A4)
1002 FORMAT(1X,1H*,20A4,1H*)
1003 FORMAT(1X,1H*,80X,1H*/1X,82(1H*))
1004 FORMAT(7(4X,A4,A2))
1005 FORMAT(7F10.0)
1006 FORMAT(7I10)
1007 FORMAT(//1X,'INITIAL VALUES OF COEFFICIENTS'/1X,30(1H=)/2X,
   1'NAME',11X,'INITIAL VALUE')
1008 FORMAT(1X,A4,A2,4(1H.),F12.4)
1009 FORMAT(//1X,'OBSERVED DATA'/1X,13(1H=)/1X,'OBS. NO.',5X,'CONCENT
   RATION',6X,'DISTANCE',9X,'TIME')
1010 FORMAT(1X,I5,6X,F12.4,4X,F12.4,4X,F12.4)
1011 FORMAT(//1X,'ITERATION'/6X,'SSQ',4X,5(7X,A4,A2))
1012 FORMAT(1X,I5,3X,F13.6,2X,5(F13.5))
1013 FORMAT(//1X,'CORRELATION MATRIX'/1X,18(1H=)/4X,10(4X,I2,5X))
1014 FORMAT(1X,I3,10(2X,F7.4,2X))
1015 FORMAT(//1X,'NON-LINEAR LEAST SQUARES ANALYSIS, FINAL RESULTS'
   1/1X,48(1H=)/62X,'95% CONFIDENCE LIMITS'/1X,'VARIABLE',4X,'NAME'
   2,8X,'VALUE',8X,'S.E.COEFF.',3X,'T-VALUE',5X,'LOWER',10X,'UPPER')
1016 FORMAT(4X,I2,6X,A4,A2,1X,F13.5,3X,F13.5,2X,F8.2,1X,F13.5,
   12X,F13.5)
1017 FORMAT(//1X,23(1H=),'ORDERED BY COMPUTER INPUT',24(1H=)/
   150X,'CONCENTRATION',16X,'RESI-'/1X,'NO',9X,'DISTANCE',12X,'TIME',
   210X,'OBS',12X,'FITTED',12X,'DUAL')
1018 FORMAT(I2,A1,F12.4,4(A1,F12.4))
1019 FORMAT(//1X,27(1H=),'ORDERED BY RESIDUAL',28(1H=)/
   150X,'CONCENTRATION',16X,'RESI-'/1X,'NO',9X,'DISTANCE',12X,'TIME',
   210X,'OBS',12X,'FITTED',12X,'DUAL')
1020 FORMAT(//1X,'END OF PROBLEM'/1X,14(1H=))
1021 FORMAT(1X,1H*,10X,'DETERMINISTIC LINEAR EQUILIBRIUM ADSORPTION FOR
   1R PULSE INJECTION',7X,1H*/1X,1H*,10X,'WITH FIRST- AND ZERO-ORDER
   2PRODUCTION AND DECAY',23X,1H*)
1022 FORMAT(1X,1H*,10X,'DETERMINISTIC TWO-SITE/TWO-REGION NONEQUILIBRI
   UM MODEL FOR ',8X,1H*/1X,1H*,10X,'PULSE-TYPE INJECTION WITH NO
2PRODUCTION OR DECAY', 23X, 1H* )

1023 FORMAT(1X, 1H*, 10X, 'STOCHASTIC TRANSPORT MODEL WITH EQUILIBRIUM AD
SORPTION', 16X, 1H*/1X, 1H*, 10X, 'ZERO-ORDER PRODUCTION AND FIRST-ORD
2ER DECAY FOR UNIFORM PULSE INPUT', 3X, 1H* )

1024 FORMAT(1X, 1H*, 10X, 'SOLUTION FOR RESIDENT CONCENTRATIONS', 34X, 1H* )

1025 FORMAT(1X, 1H*, 10X, 'SOLUTION FOR FLUX CONCENTRATIONS', 38X, 1H* )

1026 FORMAT(1X, 'C1', 8 (1H.), F12.4 )

1028 FORMAT(//1X, 'INPUT ERROR-- TOO MANY unknowns! '/'1X, 'ONE OF THE foLLOWING COEFFICIENTS MUST BE FIXED:' )

1029 FORMAT(60X, A4, A2 )

1030 FORMAT(1X, 9 (1H-1)/1X, 'NO', 9X, 'DISTANCE', 11X, 'TIME', 7X, 'CONCENTRATION')

1031 FORMAT(1X, 'INPUT ERROR: NONZERO INITIAL VALUES OF VARIABLE COEF
1FICIENTS MUST BE SPECIFIED!'//1X, 'FOR REACTION CONSTANTS BE SURE S
2IGN OF COEFFICIENT IS CORRECT AS'//1X, 'FITTING PROCEDURE WILL NOT
3CHANGE SIGNS')

1032 FORMAT(1X, 'INPUT ERROR: V, D AND R MUST BE GREATER THAN ZERO!' )

1033 FORMAT(1X, I2, 3 (A1, F12.4 )

1034 FORMAT(1X, 'CONVERGENCE CRITERIA NOT MET IN', 3X, 'ITERATIONS')

1035 FORMAT(1X, 1H*, 10X, 'NON-LINEAR LEAST-SQUARES ANALYSIS', 37X, 1H* )

1036 FORMAT(1X, 1H*, 60X, 1H* )

1037 FORMAT(1X, 1H*, 10X, 'REDUCED CONCENTRATION DATA', 44X, 1H* )

1038 FORMAT(1X, 'NO FURTHER DECREASE IN SSQ OBTAINED AFTER ', 12, ' TRIA
1LS')

1039 FORMAT(1X, 1H*, 10X, 'STOCHASTIC TRANSPORT MODEL WITH EQUILIBRIUM AD
SORPTION', 16X, 1H*/1X, 1H*, 10X, 'ZERO-ORDER PRODUCTION AND FIRST-ORD
2ER DECAY FOR UNIFORM SOLUTE LOAD', 3X, 1H* )

1040 FORMAT(1X, 1H*, 10X, 'REDUCED CONCENTRATION AND TIME DATA', 35X, 1H* )

1041 FORMAT(1X, 'RSQUARE FOR REGRESSION =', F10.8 )

1042 FORMAT(1X, 'NON-LINEAR LEAST SQUARES ANALYSIS, FINAL RESULTS
1/1X, 48 (1H-1) //54X, '95% CONFIDENCE LIMITS'//1X, 'VARIABLE', 4X, 'NAME
2, 8X, 'VALUE', 8X, 'S.E.COEFF.', 7X, 'LOWER', 10X, 'UPPER')

1043 FORMAT(4X, I2, 6X, A4, A2, 1X, F13.5, 3X, F13.5, 1X, F13.5, 2X, F13.5 )

1044 FORMAT(2I5, 6I10)

1045 FORMAT(2F10.0, I10)

1046 FORMAT(1X, 5 (1H-1), 'INFLUENT CONCENTRATIONS FOR MULTIPLE PULSES',
15 (1H-1) //5X, 'NO', 7X, 'START TIME', 9X, 'END TIME', 4X, 'CONCENTRATION')

1047 FORMAT(1X, 7 (1H-1), 'INFLUENT MASS LOADS FOR MULTIPLE PULSES',
17 (1H-1) //5X, 'NO', 7X, 'START TIME', 9X, 'M0/THETA')

1048 FORMAT(1X, I5, 3 (7X, F10.4 )

1049 FORMAT(1X, 'C0', 8 (1H.), F12.4 )

2001 FORMAT(' Enter Input file name (default=cxtfit.dat) '
2002 FORMAT(' Enter Output file name (default=cxtfit.out) '
2004 FORMAT(' Enter Plot file name (default=cxtfit.plt) '
2003 FORMAT(A15)

2006 FORMAT(' Enter Weighting Factor Code: 1=1.0 , 2=1/C^2')

2007 FORMAT(I10)

2120 FORMAT(F12.4, A1, F12.4)

STOP

END
Appendix B

Apparent Partitioning Model Code

A parameter estimation routine and a transport model have been developed based on the apparent partitioning model presented by Wise, et al. (To Be Submitted 1991). The parameter estimation routine, PARMEST, implements Marquardt's algorithm (Press, et al., 1986) in order to determine the two empirical coefficients for the modified Freundlich partitioning relationship. The Marquardt (1963) algorithm is a method of least squares parameter estimation for nonlinear models. The routine PARMEST, is designed to operate only in the inverse mode, that is, to fit the two empirical coefficients to experimental data. The model PARMSET, is designed to operate only in the forward mode, that is, to calculate an effluent history curve given a complete input data set. However, due to the empirical nature of the apparent partitioning model, PARMSET is greatly limited in its application.

Use of the Apparent Partitioning Model Code

PARMEST

The routine PARMEST requires the following input parameters in an input data set named PARMDATA:

INFILE  Input file of experimental data consisting of two columns. First column, pore volumes flushed; Second column, aqueous phase concentration
OUTFILE  Output file for resulting parameters and effluent history data
GRFFILE  Output file for importing into a plotting application, such as, CricketGraph or DeltaGraph
THETAO   Bulk oil content
THETAW   Bulk moisture content
CWI      Initial aqueous phase concentration (ML⁻³)
CWL      Lower aqueous phase concentration (ML⁻³)
ERR      Tolerance criteria
A(1)     Initial guess for the Freundlich coefficient
A(2)     Initial guess for the Freundlich exponent

An example PARMDATA data set is as follows:

<table>
<thead>
<tr>
<th>INFILE</th>
<th>data.bz</th>
</tr>
</thead>
<tbody>
<tr>
<td>OUTFILE</td>
<td>out.bz</td>
</tr>
<tr>
<td>GRFFILE</td>
<td>grf.bz</td>
</tr>
<tr>
<td>THETAO</td>
<td>0.048</td>
</tr>
<tr>
<td>THETAW</td>
<td>0.308</td>
</tr>
<tr>
<td>CWI</td>
<td>22.99</td>
</tr>
<tr>
<td>CWL</td>
<td>0.010</td>
</tr>
<tr>
<td>ERR</td>
<td>1.0E-006</td>
</tr>
<tr>
<td>A(1)</td>
<td>500.0</td>
</tr>
<tr>
<td>A(2)</td>
<td>0.800</td>
</tr>
</tbody>
</table>

The PARMDATA data set is read in free format.

**PARMSET**

The use of the model PARMSET is identical to the use of PARMEST, with the exception that the variables A(1) and A(2) are set to desired values.
Program Listing for PARMEST

The main program PARMEST, and the subroutines ASSEMB, FUNCTION, and OUTPUT are listed here. The remaining subroutine's for Marquardt's algorithm can be found in Press, et al. (1986).

PROGRAM PARMEST
*
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
CHARACTER INFIL*15,OUTFIL*15,GRFFIL*15
DOUBLE PRECISION TAU(1000),CW(1000),SIG(1000),A(5),COVAR(5,5),
  *  ALPHA(5,5),CHISQ,ALAMDA,CHINT,ERR,CWI,CWL,THETAO,THETAW
INTEGER NDATA,MA,LISTA(5),MFIT,NCA,KCWL
*
CALL ASSEMB (TAU,CW,SIG,NDATA,A,MA,LISTA,MFIT,NCA,ALAMDA,
  *  INFIL,OUTFIL,GRFFIL,ERR,CWI,CWL,THETAO,THETAW)
*

CHINT = 10000.0
DO 100 I=1,10000
   CALL MRQMIN (TAU,CW,SIG,NDATA,A,MA,LISTA,MFIT,COVAR,
     *  ALPHA,NCA,CHISQ,FUNCS,ALAMDA,CWI,CWL,THETAO,THETAW)
   IF (CHISQ.EQ.CHINT) GOTO 100
   IF (ABS(CHINT-CHISQ).LE.ERR) GOTO 200
   CHINT = CHISQ
100 CONTINUE
*
200 CALL OUTPUT (I,TAU,CW,NDATA,A,MA,INFIL,OUTFIL,GRFFIL,CHISQ,
  *  ERR,CWI,CWL,THETAO,THETAW)
*
PAUSE
END
*

SUBROUTINE ASSEMB (TAU,CW,SIG,NDATA,A,MA,LISTA,MFIT,NCA,
  *  ALAMDA,INFIL,OUTFIL,GRFFIL,ERR,CWI,CWL,THETAO,THETAW)
*
PARAMETER (K=1000,L=5)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
CHARACTER INFIL*15,OUTFIL*15,GRFFIL*15,DUMMY*15
DOUBLE PRECISION TAU(K),CW(K),SIG(K),A(L),ALAMDA,
  *  ERR,CWI,CWL,THETAO,THETAW
INTEGER NDATA,MA,LISTA(L),MFIT,NCA,NO
*
MA = 2
MFIT = 2
NCA = 5
*
OPEN(14,FILE='PARMDATA')
READ(14,*) DUMMY, INFILE
READ(14,*) DUMMY, OUTFILE
READ(14,*) DUMMY, GRFFILE
READ(14,*)
READ(14,*) DUMMY, THETAO
READ(14,*) DUMMY, THETAW
READ(14,*) DUMMY, CWI
READ(14,*) DUMMY, CWL
READ(14,*)
READ(14,*) DUMMY, ERR
READ(14,*) DUMMY, A(1)
READ(14,*) DUMMY, A(2)
CLOSE (14)

* 10 WRITE(*,*) 'NO. - PARAMETER - CURRENT VALUE'
   WRITE(*,*)
   WRITE(*,*) ' 1 INFILF ', INFILF
   WRITE(*,*) ' 2 OUTFILF ', OUTFILF
   WRITE(*,*) ' 3 GRFFILE ', GRFFILE
   WRITE(*,938) THETAO
   WRITE(*,939) THETAW
   WRITE(*,940) CWI
   WRITE(*,941) CWL
   WRITE(*,942) ERR
   WRITE(*,943) A(1)
   WRITE(*,944) A(2)
   WRITE(*,*)
   WRITE(*,*) ' 0 NO CHANGE'

* WRITE(*,*)
   WRITE(*,*) 'ENTER THE PARAMETER NO. YOU WISH TO CHANGE, OR ZERO.'
   READ(*,*)NO
   WRITE(*,*)
   IF (NO.EQ.0) GOTO 15
   IF (NO.EQ.1) THEN
      WRITE(*,*) 'ENTER INFILF'
      READ(*,*) INFILF
   ENDIF
   IF (NO.EQ.2) THEN
      WRITE(*,*) 'ENTER OUTFILF'
      READ(*,*) OUTFILF
   ENDIF
   IF (NO.EQ.3) THEN
      WRITE(*,*) 'ENTER GRFFILE'
      READ(*,*) GRFFILE
   ENDIF
   IF (NO.EQ.4) THEN
      WRITE(*,*) 'ENTER THETAO'
      READ(*,*) THETAO
   ENDIF
   IF (NO.EQ.5) THEN
      WRITE(*,*) 'ENTER THETAW'
      READ(*,*) THETAW
   ENDIF
   IF (NO.EQ.6) THEN
      WRITE(*,*) 'ENTER CWI'
READ(*,*) CWI
ENDIF
IF (NO.EQ.7) THEN
  WRITE(*,*) 'ENTER CWL'
  READ(*,*) CWL
ENDIF
IF (NO.EQ.8) THEN
  WRITE(*,*) 'ENTER ERR'
  READ(*,*) ERR
ENDIF
IF (NO.EQ.9) THEN
  WRITE(*,*) 'ENTER INITIAL GUESS FOR A(1)'
  READ(*,*) A(1)
ENDIF
IF (NO.EQ.10) THEN
  WRITE(*,*) 'ENTER INITIAL GUESS FOR A(2)'
  READ(*,*) A(2)
ENDIF
WRITE(*,950)
GOTO 10
*
15 OPEN(14,FILE='PARMDATA')
WRITE(14,*)' INFILE ','INFILE
WRITE(14,*)' OUTFILE ','OUTFILE
WRITE(14,*)' GRFFILE ','GRFFILE
WRITE(14,*)
WRITE(14,*)' THETA0 ','THETA0
WRITE(14,*)' THETAW ','THETAW
WRITE(14,*)' CWI ','CWII
WRITE(14,*)' CWL ','CWL
WRITE(14,*)
WRITE(14,*)' ERR ','ERR
WRITE(14,*)' A(1) ','A(1)
WRITE(14,*)' A(2) ','A(2)
CLOSE (14)
*
OPEN (15,FILE=INFILE)
NDATA = 0
DO 20 I=1,1000
  SIG(I) = 1.0
  READ(15,*,END=25) TAU(I),CW(I)
  NDATA = NDATA + 1
20 CONTINUE
25 CLOSE (15)
*
LISTA(1) = 1
DO 30 I=2,MA
  LISTA(I) = I
30 CONTINUE
*
ALAMDA = -1.0
*
938 FORMAT (' 4 THETA0 ','F10.4)
939 FORMAT (' 5 THETAW ','F10.4)
940 FORMAT (' 6 CWI ','F10.4)
941 FORMAT (' 7 CWL ','F10.4)
942 FORMAT (' 8       ERR       ',F12.6)
943 FORMAT (' 9       A(1)       ',F6.0)
944 FORMAT ('10       A(2)       ',F10.4)
950 FORMAT (//////////////)
RETURN
END

*     *
*     SUBROUTINE FUNCTION (TAU,A,CW,DCWDA,NA,CWI,CWL,
*                          THETAO,THETAW,KMIN)
*     *
*     THIS FUNCTION ASSUMES A FREUNDlich PARTITIONING
*     ie. CW = Gamma * Co^Delta
*     A(1)=GAMMA & A(2)=DELTA
*     *
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
DOUBLE PRECISION A(NA),DCWDA(NA)
*     G = A(1)
D = A(2)
TAUPL = 1.0 + (THETAO/THETAW*G*D*CWI**((D-1.0)))
IF (TAU.LE.TAUPL) THEN
   CW = CWI
   DCWDA(1) = 0.0
   DCWDA(2) = 0.0
RETURN
ENDIF
IF (KMIN.EQ.1) THEN
   CW = CWL
   DCWDA(1) = 0.0
   DCWDA(2) = 0.0
RETURN
ENDIF
CW=((TAU-1.0)*THETAW/(G*D*THETAO))**((1.0/(D-1.0))
CST1 = (((TAU-1.0)*THETAW/(D*THETAO))**((1.0/(D-1.0)))
DCWDA(1)= CST1*(-1.0/(D-1.0))*G**(-D/(D-1.0))
CST2 = (((TAU-1.0)*THETAW)/(G*D*THETAO))
DCWDA(2)= (-1.0/(D-1.0))*(1.0/D)*CST2**(1.0/(D-1.0)) -
           (1.0/(D-1.0)**2)*CST2**(1.0/(D-1.0))*DLOG(CST2)

*     IF (CW.LT.CWL) THEN
   KMIN = 1
   CW = CWL
   DCWDA(1) = 0.0
   DCWDA(2) = 0.0
ENDIF
*
RETURN
END

*     *
*     SUBROUTINE OUTPUT (I,TAU,CW,NDATA,A,MA,INFILE,OUTFILE,GRFILE,
*                      CHISQ,ERR,CWI,CWL,THETAO,THETAN)
*     *
CHARACTER INFILE*15,OUTFILE*15,GRFILE*15
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
DOUBLE PRECISION TAU(1000), CW(1000), CALCCW(1000), A(5)

OPEN (16, FILE=OUTFILE)
WRITE (16, '*') ' INPUT PARAMETERS:'
WRITE (16, 900) INFILE
WRITE (16, 901) OUTFILE
WRITE (16, 902) GRFFILE
WRITE (16, 903) THETAO
WRITE (16, 904) THETAW
WRITE (16, 905) CWI
WRITE (16, 906) CWL
WRITE (16, 907) ERR
WRITE (16, '*')
WRITE (16, '*') ' RESULTS:'
WRITE (16, 909) I
WRITE (16, 916) CHISQ
DO 10 J=1, MA
   WRITE (16, 910) J, A(J)
10 CONTINUE
WRITE (16, 917)

OPEN (17, FILE=GRFFILE)
WRITE (17, 911)
WRITE (17, 912) CHAR(9), CHAR(9)

G = A(1)
D = A(2)
TAUPL = 1.0 + (THETAO/THETAW*G*D*CWI**((D-1.0)))
DO 20 K=1, NDATA
   IF (TAU(K) .LE. TAUPL) THEN
      CALCCW(K) = CWI
   ELSE
      CALCCW(K) = ((TAU(K) - 1.0) * THETAW) / (G * D * THETAO)) ** (1.0 / (D-1.0))
      IF (CALCCW(K) .LT. CWL) THEN
         CALCCW(K) = CWL
   ENDIF
   WRITE (16, 915) TAU(K), CHAR(9), CW(K), CHAR(9), CALCCW(K)
20 CONTINUE

900 FORMAT (/5X, ' INFILE = ', A15)
901 FORMAT (5X, 'OUTFILE = ', A15)
902 FORMAT (5X, 'GRFFILE = ', A15)
903 FORMAT (5X, ' THETAO = ', F10.6)
904 FORMAT (5X, ' THETAW = ', F10.6)
905 FORMAT (5X, ' CWI = ', F10.6)
906 FORMAT (5X, ' CWL = ', F10.6)
907 FORMAT (5X, ' ERR = ', F10.6)
909 FORMAT (/6X, 'NO. OF CALLS ON MRQMIN = ', I4)
910 FORMAT (6X, 'A1', I2, ') = ', F15.6)
911 FORMAT ('**')
912 FORMAT ('TAU (pore volumes), A1, DATA, A1, MODEL')
915 FORMAT (F12.6, A1, F12.6, A1, F12.6)
916 FORMAT (6X, 'CHISQ = ', F10.4)
917 FORMAT (/, ' TAU ', ', ', DATA ', ', ', MODEL')
* 
CLOSE (16)
CLOSE (17)
RETURN
END
Program Listing for PARMSET

The main program PARMSET and the subroutines ASSEMB and OUTPUT are listed here. This is an entire listing of this code.

```
PROGRAM PARMSET

*  IMPLICIT DOUBLE PRECISION (A-H,O-Z)
  CHARACTER INFILE*15,OUTFILE*15,GRFFILE*15
  DOUBLE PRECISION TAU(1000),CW(1000),A(5),
  *  CHISQ,CWI,CWL,THETAO,THETAW
  INTEGER  NDATA,MA,LISTA(5),MFIT,NCA,KCWL
  *
  11 CALL ASSEMB (TAU,CW,NDATA,A,MA,
      *  INFILE,OUTFILE,GRFFILE,CWI,CWL,THETAO,THETAW)
  *
  *
  200 CALL OUTPUT (TAU,CW,NDATA,A,MA,INFILE,OUTFILE,GRFFILE,CHISQ,
      *  CWI,CWL,THETAO,THETAW)
  *
  PAUSE
  GOTO 11
END

*

SUBROUTINE ASSEMB (TAU,CW,NDATA,A,MA,
*  INFILE,OUTFILE,GRFFILE,CWI,CWL,THETAO,THETAW)
*
PARAMETER (K=1000,L=5)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
CHARACTER INFILE*15,OUTFILE*15,GRFFILE*15,DUMMY*15
DOUBLE PRECISION TAU(K),CW(K),A(L),
*  CWI,CWL,THETAO,THETAW
INTEGER  NDATA,MA,NO
*
MA = 2
*
OPEN(14,FILE='PARMDATA')
READ(14,*)DUMMY,INFILE
READ(14,*)DUMMY,OUTFILE
READ(14,*)DUMMY,GRFFILE
READ(14,*)
READ(14,*)DUMMY,THETAO
READ(14,*)DUMMY,THETAW
READ(14,*)DUMMY,CWI
READ(14,*)DUMMY,CWL
READ(14,*)
READ(14,*)DUMMY,ERR
READ(14,*)DUMMY,A(1)
READ(14,*)DUMMY,A(2)
```
CLOSE (14)

10 WRITE(*,*) 'NO. - PARAMETER - CURRENT VALUE'
WRITE(*,*)
WRITE(*,*) 1 INFILE ',INFILE
WRITE(*,*) 2 OUTFILE ',OUTFILE
WRITE(*,*) 3 GRFILE ',GRFILE
WRITE(*,938) THETA0
WRITE(*,939) THETAW
WRITE(*,940) CWI
WRITE(*,941) CWL
WRITE(*,942) ERR
WRITE(*,943) A(1)
WRITE(*,944) A(2)
WRITE(*,*)
WRITE(*,*) 0 NO CHANGE'

WRITE(*,*)
WRITE(*,*) 'ENTER THE PARAMETER NO. YOU WISH TO CHANGE, OR ZERO.'
READ(*,*) NO
WRITE(*,*)
IF (NO.EQ.0) GOTO 15
IF (NO.EQ.1) THEN
    WRITE(*,*) 'ENTER INFILE'
    READ(*,*) INFILE
ENDIF
IF (NO.EQ.2) THEN
    WRITE(*,*) 'ENTER OUTFILE'
    READ(*,*) OUTFILE
ENDIF
IF (NO.EQ.3) THEN
    WRITE(*,*) 'ENTER GRFILE'
    READ(*,*) GRFILE
ENDIF
IF (NO.EQ.4) THEN
    WRITE(*,*) 'ENTER THETA0'
    READ(*,*) THETA0
ENDIF
IF (NO.EQ.5) THEN
    WRITE(*,*) 'ENTER THETAW'
    READ(*,*) THETAW
ENDIF
IF (NO.EQ.6) THEN
    WRITE(*,*) 'ENTER CWI'
    READ(*,*) CWI
ENDIF
IF (NO.EQ.7) THEN
    WRITE(*,*) 'ENTER CWL'
    READ(*,*) CWL
ENDIF
IF (NO.EQ.8) THEN
    WRITE(*,*) 'ENTER ERR'
    READ(*,*) ERR
ENDIF
IF (NO.EQ.9) THEN
    WRITE(*,*) 'ENTER VALUE FOR A(1)'

READ(*,*)A(1)
ENDIF
IF (NO.EQ.10) THEN
   WRITE(*,*)'ENTER VALUE FOR A(2)'
   READ(*,*)A(2)
ENDIF
WRITE(*,950)
GOTO 10

* 15 OPEN(14,FILE='PARMDATA')
   WRITE(14,*)' INFILE ',INFILE
   WRITE(14,*)' OUTFILE ',OUTFILE
   WRITE(14,*)' GRFFILE ',GRFFILE
   WRITE(14,*)' THETAO ',THETAO
   WRITE(14,*)' THETAW ',THETAW
   WRITE(14,*)' CWI ',CWI
   WRITE(14,*)' CWL ',CWL
   WRITE(14,*)' ERR ',ERR
   WRITE(14,*)' A(1) ',A(1)
   WRITE(14,*)' A(2) ',A(2)
CLOSE (14)

* OPEN (15,FILE=INFILE)
   NDATA = 0
   DO 20 I=1,1000
      READ(15,*,END=25) TAU(I),CW(I)
      NDATA = NDATA + 1
   20 CONTINUE
CLOSE (15)

938 FORMAT (' 4  THETAO ',F10.4)
939 FORMAT (' 5  THETAW ',F10.4)
940 FORMAT (' 6  CWI ',F10.4)
941 FORMAT (' 7  CWL ',F10.4)
942 FORMAT (' 8  ERR ',F12.6)
943 FORMAT (' 9  A(1) ',F6.0)
944 FORMAT ('10  A(2) ',F10.4)
950 FORMAT ('/-----------------/
RETURN
END

* *
* *
* SUBROUTINE OUTPUT (TAU,CW,NDATA,A,MA,INFILE,OUTFILE,GRFFILE,
* CHISQ,CWI,CWL,THETAO,THETAW)
* *
CHARACTER INFILE*15,OUTFILE*15,GRFFILE*15
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
DOUBLE PRECISION TAU(1000),CW(1000),CALCCW(1000),A(5)

* OPEN (16,FILE=OUTFILE)
WRITE(16,*)' INPUT PARAMETERS:'
WRITE(16,900)INFILE
WRITE(16,901)OUTFILE

WRITE(16,902)GRFFILE
WRITE(16,903)THETA0
WRITE(16,904)THETA
WRITE(16,905)CWI
WRITE(16,906)CWL
WRITE(16,*)
DO 10 J=1,MA
   WRITE(16,910)J,A(J)
10 CONTINUE
WRITE(16,*)
WRITE(16,*),' RESULTS:'
*
OPEN (17,FILE=GRFFILE)

CHISQ = 0.0
G = A(1)
D = A(2)
TAUPL = 1.0 + (THETA0/THETAN*G*D*CWI**((D-1.0))
TAUL = 1.0 + (THETA0/THETAN*G*D*CWL**((D-1.0))
DO 20 K=1,NDATA
   IF (TAU(K).LE.TAUPL) THEN
      CALCCW(K) = CWI
   ELSE
      IF (TAU(K).GE.TAUL) THEN
         CALCCW(K) = CWL
      ELSE
         CALCCW(K) = ((TAU(K)-1.0)*THETAW)/(G*D*THETA0)**(1.0/(D-1.0))
      ENDIF
   ENDIF
20 CONTINUE

DY = (CW(K)-CALCCW(K))
CHISQ = CHISQ + DY * DY

AMASS = CWI * TAUPL * 29.4/1000.
CMASS = CWL * (1000.0 - TAUPL) * 29.4/1000.
CONST = (THETAW/(THETAN*G*D))**(1.0/(D-1.0)) * 29.4/1000.
BMASSE1 = CONST * (D-1.0)/D * (TAUL - 1.0)**(D/(D-1.0))
BMASSE2 = CONST * (D-1.0)/D * (TAUPL - 1.0)**(D/(D-1.0))
BMASS = BMASSE1 + BMASSE2
TOTMASS = AMASS + BMASS + CMASS
OPEN (18,FILE='MASSFILE')
WRITE(18,911)
WRITE(18,913)CHAR(9),CHAR(9)
DO 40 L=0,1200,10
   X = L * 1.0
   IF (X.LE.TAUPL) THEN
      CUMMASS = X * CWI * 29.4/1000.
   ELSE
      IF (X.GE.TAUL) THEN
         CUMMASS = AMASS + BMASS + (X - TAUPL) * CWL * 29.4/1000.
      ELSE
         CUMMASS = AMASS + (CONST*(D-1.0)/D*(X-1.0)**(D/(D-1.0))
                        -BMASSE2)
      ENDIF
   ENDIF
40 CONTINUE
FCTMASS = CUMMASS / TOTMASS
WRITE (18,915) X,CHAR(9),CUMMASS,CHAR(9),PCTMASS
40 CONTINUE
*
WRITE (16,918) TAUPL
WRITE (16,919) TAUL
WRITE (16,916) CHISQ
WRITE (16,917)
WRITE (17,911)
WRITE (17,912) CHAR(9),CHAR(9)
DO 30 K=1,NDATA
WRITE (16,915) TAU(K),CHAR(9),CW(K),CHAR(9),CALCCW(K)
WRITE (17,915) TAU(K),CHAR(9),CW(K),CHAR(9),CALCCW(K)
30 CONTINUE
WRITE (*,*),' AMASS = ',AMASS
WRITE (*,*),' BMASS = ',BMASS
WRITE (*,*),' CMASS = ',CMASS
WRITE (*,*),' TAUPL = ',TAUPL
WRITE (*,*),' TAUL = ',TAUL
WRITE (*,*),' CHISQ = ',CHISQ
*
900 FORMAT (/,'INFILE = ',A15)
901 FORMAT (5X,'OUTFILE = ',A15)
902 FORMAT (5X,'GRFFILE = ',A15)
903 FORMAT (5X,'THETAO = ',F10.6)
904 FORMAT (5X,'THETAW = ',F10.6)
905 FORMAT (5X,'CWI = ',F10.6)
906 FORMAT (5X,'CWL = ',F10.6)
910 FORMAT (7X,'A(','I2,') = ',F12.6)
911 FORMAT ('(*)'
912 FORMAT ('TAU (pore volumes) = ',A1,'DATA',A1,'MODEL')
913 FORMAT ('TAU (pore volumes) = ',A1,'CUMMASS',A1,'PCTMASS')
915 FORMAT (F15.6,A1,F15.6,A1,F15.6)
916 FORMAT (6X,'CHISQ = ',F10.4)
917 FORMAT ('/',A,'TAU = ',A,DATA,'MODEL',/)
918 FORMAT (/,'TAUPL = ',F10.4)
919 FORMAT (6X,'TAUL = ',F10.4)
*
CLOSE(16)
CLOSE(17)
RETURN
END
Appendix C

Numerical 1-D Model Code

The numerical 1-D model code developed by Kool, et al. (1989) for evaluating break through curves has been modified in two ways. First, the three cation exchange relationships have been replaced by three "partitioning" relationships: linear, Langmuir, and Freundlich. Second, the code has been modified for more convenient use.

Kool Code Modifications

The original Kool code, "BTFIT", was written in FORTRAN. The code has been modified and compiled for execution on a Mac II. Modifications were made only to the main program and the function SLOPE. The modifications are as follows:

1. A new plot file option was added. The new plot file option writes the pore volumes flushed and the calculated concentration for each observation time. A tab delimiter is written between the two output variables which allows the plot file to easily be imported into a plotting application, e.g., CricketGraph or DeltaGraph.

2. Unit numbers 5 and 6 were changed to 15 and 16, respectively.
3. An option was added to weight the sum of the squared residuals by $1/c^2$, with $c$ being the observed aqueous concentration.

4. Tab delimiters were included in the write statements of the output file.

5. The three isotherms incorporated in the function SLOPE have been replaced with three partitioning relationships: linear, Langmuir, and Freundlich.

**Use of the Modified Kool Model Code**

The use of the modified model is identical to that of the original model with the exception that a weighting function must be specified following entry of the input data set filename and the variable MODE has been redefined. The variable MODE, originally for specifying the type of exchange reaction, is now for specifying the type partitioning relationship. The three modes are defined as follows:

<table>
<thead>
<tr>
<th>MODE</th>
<th>Relationship</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Linear</td>
</tr>
<tr>
<td>2</td>
<td>Langmuir</td>
</tr>
<tr>
<td>3</td>
<td>Freundlich</td>
</tr>
</tbody>
</table>

The other necessary input parameters are defined in Chapter 3 of this work.
**Modified Main Program Listing and Function SLOPE**

The modified main program and the function SLOPE code listings are included here. Code modifications are preceded and followed by the comment line CGCR. The subroutines and functions which were not modified are not included here but are available from:

HydroGeoLogic, Inc.
503 Carlisle Drive, Suite 250
Herndon, VA  22070

```
C
C
C
C
C
C
C
C
C
C
C

***********************************************************************
*                                                             *
*  NON-LINEAR LEAST-SQUARES ANALYSIS OF BREAKTHROUGH CURVES  *
*  FOR SINGLE SPECIES PARTITIONING BETWEEN RESIDUAL OIL       *
*  AND MOBILE WATER PHASES                                    *
*                                                             *
*  THIS IS A MODIFIED VERSION OF J.B. KOOL'S PROGRAM FOR      *
*  CATION EXCHANGE, 1987                                      *
*                                                             *
*  MODIFIED BY G.C. ROBINSON, 3/18/91                         *
*                                                             *
***********************************************************************

PROGRAM RSFIT
IMPLICIT REAL*8(A-H,O-Z)
REAL*4 Y(100),F(100),DELZ(100,7),X,BMAX(7),BMIN(7),B(7),DELT
1,CI,C0,CT,TP,TOL
DIMENSION R(100),TH(14),TB(14),E(7),Q(7),F(7),PHI(7),A(7,7),D(7,7)
1,PORV(100)
COMMON/MODAT1/X(100),INDEX(7),NOB,NN,NSTEPS,DELT,DEL,T,CI,C0,CT
1,TP,TOL
CHARACTER TITLE*72, BI(7)*8
CHARACTER*25 FILIN,FILOUT,FILGRF
DATA STOPCR/5.0D-04/,ZERO/0D0/,NVAR/6/
C
C
C
C
C

WRITE(*,*) ' ENTER INPUT-FILE NAME ------>'
READ(*,*) FILIN
C
CGCR

WRITE(*,2006)
```
READ(*,2007) IWF
IF (IWF.EQ.2) GOTO 1
IWF=1

CGCR
C
1 WRITE(*,*), ' ENTER OUTPUT-FILE NAME ------>
READ(*,*) FILOUT
CGCR
WRITE(*,*), ' ENTER GRAPH-FILE NAME ------>
READ(*,*) FILGRF
CALL TIME(TIME1)
OPEN(15,FILE=FILIN,STATUS='OLD')
OPEN(16,FILE=FILOUT,STATUS='NEW')
OPEN(17,FILE=FILGRF,STATUS='NEW')

CGCR
C
-----
C NCASES = NO. OF PROBLEMS TO BE SOLVED
C
-----
READ (15,'(I5)') NCASES
DO 150 NCASE=1,NCASES
C
----- READ INPUT PARAMETERS ------
WRITE(16,1000)

-----
C TITLE = DESCRIPTIVE TITLE FOR PROBLEM (2 LINES)
C
-----
DO 2 I=1,2
READ(15,'(A)') TITLE
2 WRITE(16,1001) TITLE
WRITE(16,1002)

-----
C NN = NUMBER OF NODES IN DOMAIN FOR FINITE DIFFERENCE TRANSPORT
C SOLUTION
C NSTEPS = MAXIMUM NUMBER OF TIME STEPS PERMITTED IN FD TRANSPORT SOL
C NOB = NUMBER OF OBSERVATIONS TO BE FITTED
C MIT = MAX NUMBER OF ITERATIONS (MIT=0 SOLVES DIRECT PROBLEM only
C MAXTRY = MAX TRIAL SOLUTIONS AT ITERATION BEFORE QUITING
C SUGGEST 10 TO 50, SMALLER VALUES REDUCE RUN TIME
C BUT MAY MISS CONVERGENT SOLUTION
C MODE = SPECIFIES TYPE OF EXCHANGE REACTION
CGCR
C = 1: LINEAR PARTITIONING
C = 2: LANGMUIR PARTITIONING
C = 3: FREUNDLICH PARTITIONING
CGCR
-----
READ(15,1006) NN,NSTEPS,NOB,MAXTRY,MIT,MODE
-----
C CLENGT = COLUMN LENGTH
C DELT = CONSTANT TIME STEP
C CI = INITIAL CONCENTRATION, (IN THE PORE WATER PHASE)
C C0 = FEED CONCENTRATION
C CT = TOTAL CONCENTRATION
C TP = PULSE DURATION
C TOL = CONVERGENCE CRITERION FOR FD SOLUTION
C
-----
READ(15,1005)CLENGT,DELT,CI,C0,CT,TP,TOL
DELX=CLENGT/FLOAT(NN-1)
WRITE(16,1036)NN,NSTEPS,DELX,DELT,TP,CI,C0,CT,TOL
IF (MTRY.EQ.0) MTRY=10
C
C ------ INPUT PARAMETERS FOR MODEL, ORDERED:
C
CGCR
C WC   = WATER CONTENT
C RHO  = RESIDUAL OIL CONTENT
C V    = POKE WATER VELOCITY
C D    = DISPERSION COEFFICIENT
C AK   = COEFFICIENT
C ST   = EXPONENT
CGCR
C ----
READ(15,1004) (BI(I),I=1,NVAR)
C
C ------- READ INITIAL ESTIMATES -------
READ(15,1005) (B(I),I=1,NVAR)
C
C ------- READ INDICES -------
INDEX = 0 PARAMETER IS HELD CONSTANT
INDEX = 1 ' ' IS OPTIMIZED
C ----
READ(15,1006) (INDEX(I),I=1,NVAR)
C
C ------- READ CONSTRAINTS ON PARAMETER VALUES
C BMN AND BMX ARE MIN AND MAX CONSTRAINTS
C BMN(I)=BMX(I)=0 WILL OMIT CONSTRAINT ON PARAMETER I
C ----
READ(15,1005) (BMN(I),I=1,NVAR)
READ(15,1005) (BMX(I),I=1,NVAR)
5 CONTINUE
C
C ------- WRITE EXPERIMENTAL DATA -------
C X IS THE INDEPENDENT VARIABLE (= TIME)
C Y IS THE DEPENDENT VARIABLE (= EFFLUENT CONCENTRATION)
C ----
DO 10 I=1,NOB
READ(15,'(2F10.0)') X(I),Y(I)
10 WRITE(16,'(2F10.5)') X(I),Y(I)
C
C ------- REARRANGE VARIABLE ARRAYS -------
NU1=NVAR+1
NU2=2*NVAR
18 NP=0
DO 20 I=NU1,NU2
   II=I-NVAR
   TB(I)=DBLE(B(II))
   IF(INDEX(II).EQ.0) GO TO 20
   NP=NP+1
   BI(NP)=BI(II)
   B(NP)=B(II)
   TB(NP)=DBLE(B(II))
   TH(NP)=DBLE(B(NP))
   BMIN(NP)=BMIN(II)
   BMAX(NP)=BMAX(II)
   20 TH(I)=DBLE(B(II))

C
C       ------ EVALUATE INITIAL RESIDUAL VECTOR R ------
C GA=2.0D-02
NIT=0
CALL MODEL(TH,F,MODE)
IF (NIT.EQ.0) GO TO 140
SSQ=ZERO
DO 32 I=1,NOB
   R(I)=DBLE(Y(I)-F(I))
CGCR
   IF (IWF.EQ.2) R(I)=R(I)/DBLE(Y(I))
CGCR
   SSQ=SSQ+R(I)*R(I)
   IF(NP.EQ.0.OR.NIT.EQ.0) THEN
      WRITE(16,1011)
      WRITE(16,1012) NIT,SSQ
      GO TO 110
   ELSE
      WRITE(16,1011) (BI(J),J=1,NP)
      WRITE(16,1012) NIT,SSQ,(B(I),I=1,NP)
   ENDIF
C
C       ------ EVALUATE JACOBIAN: J(i,j) = dR(i)/dTH(j) ------
C NIT=NIT+1
   NTRIAL=0
   GA=0.1D0*GA
   DO 38 J=1,NP
   IF(NIT.EQ.1) E(J)=1.0D0
   TEMP=TH(J)
   TH(J)=1.0D0*TH(J)
   Q(J)=ZERO
   CALL MODEL(TH,DELZ(I,J),MODE)
   DO 36 I=1,NOB
CGCR
   IF (IWF.EQ.1) DELZ(I,J)=DELZ(I,J)-F(I)
   IF (IWF.EQ.2) DELZ(I,J)=(DELZ(I,J)-F(I))/Y(I)
CGCR
   C
   C       ------ FORM Q = J'*R AND D = J'*J ------
C 36 Q(J)=Q(J)+DBLE(DELZ(I,J))*R(I)
   Q(J)=100.D0*Q(J)/TEMP
   38 TH(J)=TEMP
   DO 44 I=1,NP

DO 42 J=1,I
   SUM=ZERO
DO 40 K=1,NOB
40  SUM=SUM+DBLE (DELZ(K,I)*DELZ(K,J))
   D(I,J)=1.0D0*SUM/(TH(I)*TH(J))
42  D(J,I)=D(I,J)

----- E IS SCALING VECTOR -----
   SCAL=DSQRT (DMAX1(D(I,I),1.0D-30))
   E(I)=DMAX1(E(I),SCAL)
50  DO 52 I=1,NP
   DO 52 J=1,NP

----- A IS SCALED J'*J ----- 
   A(I,J)=D(I,J)/(E(I)*E(J))
54  DO 54 I=1,NP
   P(I)=Q(I)/E(I)
   PHI(I)=P(I)

----- GA IS LEVENBERG-MARQUARDT PARAMETER ----- 
58  A(I,I)=A(I,I)+GA
   CALL QRSOLV(A,NP,P)

----- P/E IS THE CORRECTION VECTOR ----- 
   STEP=1.0D0
62  DO 62 I=1,NP
   TB(I)=P(I)*STEP/E(I)+TH(I)
   IF(BMIN(I).EQ.BMAX(I)) GO TO 58
   IF(TB(I).GT.DBLE(BMAX(I))) TB(I)=DBLE(BMAX(I))
   IF(TB(I).LT.DBLE(BMIN(I))) TB(I)=DBLE(BMIN(I))
   P(I)=(TB(I)-TH(I))*E(I)/STEP
66  CONTINUE
60  DO 60 I=1,NP
   IF(TH(I)*TB(I))66,66,62
64  CONTINUE
   SUMB=ZERO

----- CHECK IF STEP IS SATISFACTORY ----- 
   CALL MODEL(TB,F,MODE)
68  DO 68 I=1,NOB
   R(I)=DBLE(Y(I)-F(I))
   CGCR
   IF (IWF.EQ.2) R(I)=R(I)/DBLE(Y(I))
64  SUMB=SUMB+R(I)*R(I)
   SUM1=ZERO
   SUM2=ZERO
   SUM3=ZERO
   DO 68 I=1,NP
   SUM1=SUM1+P(I)*PHI(I)
   SUM2=SUM2+P(I)*P(I)
   SUM3=SUM3+PHI(I)*PHI(I)
68  ARG=ZERO
   IF(SUM2*SUM3.NE.ZERO) ARG=SUM1/DSQRT(SUM2*SUM3)
   ARG1=ZERO
   IF(NP.GT.1) ARG1=DSQRT(1.-ARG*ARG)
ANGLE=57.29578D0*DATAN2(ARG1,ARG)

C
C
DO 72 I=1,NP
IF(TH(I)*TB(I))74,74,72
72 CONTINUE
NTRIAL=NTRIAL+1
IF(NTRIAL.GT.MAXTRY) GO TO 95
IF(SUMB/SSQ-1.0D0) 80,80,74
74 IF(ANGLE-30.0D0)76,76,78

C
C
------ CORRECT STEP LENGTH AND L-M PARAMETER ------
76 STEP=0.5D0*STEP
GO TO 56
78 GA=10.0D0*GA
GO TO 50

C
C
------ PRINT COEFFICIENTS AFTER EACH ITERATION ------
80 CONTINUE
DO 82 I=1,NP
82 TH(I)=TB(I)
WRITE(16,1012) NIT,SUMB,(TH(I),I=1,NP)
DO 86 I=1,NP
IF(DABS(P(I)*STEP/E(I))/(1.0D-20+DABS(TH(I))))-STOCR) 86,86,94
86 CONTINUE
GO TO 96
94 SSQ=SUMB
IF(NIT.LT.MIT) GO TO 34
IF(NIT.EQ.MIT) WRITE(16,1034) MIT
GO TO 96
95 WRITE(16,1038) MAXTRY

C
C
------ INVERT J'*J TO OBTAIN PARAMETER CORRELATIONS ------
96 CONTINUE
CALL MATINV(D,NP)

C
C
------ WRITE CORRELATION MATRIX ------
DO 98 I=1,NP
98 E(I)=DSQRT(DMAX1(D(I,I),1.0D-30))
IF(NP.EQ.1) GO TO 104
WRITE(16,1013) (I,I=1,NP)
DO 102 I=1,NP
DO 100 J=1,I
100 A(J,I)=D(J,I)/(E(I)*E(J))
102 WRITE(16,1014) I,(A(J,I),J=1,I)

C
C
------ CALCULATE REGRESSION COEFFICIENT
104 SUM1=ZERO
SUM2=ZERO
DO 106 I=1,NOB
SUM1=SUM1+DBLE(Y(I))
106 SUM2=SUM2+DBLE(Y(I)*Y(I))
RSQ=1.-SUMB/(SUM2-SUM1*SUM1/NOB)
WRITE(16,1041) RSQ

C
C
------ CALCULATE 95% CONFIDENCE INTERVAL ------
Z=1./DBLE(NOB-NP)
SDEV=DSQRT(Z*SUNB)
TVAR=1.96+Z*(2.3779+Z*(2.7135+Z*(3.187936+2.466666*Z**2)))
WRITE(16,1015)
DO 108 I=1,NP
SECOEF=E(I)*SDEV
TVALUE=TH(I)/SECOEF
TSEC=TVAR*SECOEF
TMCOE=TH(I)-TSEC
TPOCOE=TH(I)+TSEC
WRITE(16,1016) I,BI(I),TH(I),SECOEF,TVALUE,TMCOE,TPOCOE
108 CONTINUE
C
C ------ PREPARE FINAL OUTPUT ------
110 WRITE(16,1017)
DO 116 I=1,NB
CGCR
116 WRITE(16,1018) I,CHAR(9),X(I),CHAR(9),Y(I),CHAR(9),F(I)
111 CHAR(9),R(I)
DO 210 I=1,NB
PORV(I) = B(3) * X(I) / CLEN
T
210 WRITE(17,1210)PORV(I),CHAR(9),F(I)
GO TO 150
140 WRITE(16,1030)
DO 145 I=1,NB
141 WRITE(16,1033)I,CHAR(9),X(I),CHAR(9),F(I)
142 DO 220 I=1,NB
143 PORV(I) = B(3) * X(I) / CLEN
144 WRITE(17,1210)PORV(I),CHAR(9),F(I)
150 CONTINUE
CALL TIME(TIME2)
DTIME = (TIME2-TIME1)
WRITE(*,1050)DTIME
PAUSE 'Hit return to continue ...
'
CGCR
C
C ------ END OF PROBLEM ------
1000 FORMAT(/1X,'INITIAL VALUES OF COEFFICIENTS'/5X,30(1H=)/5X,
1 'NAME',7X,' VALUE',6X,' INDEX',6X,'LOWER',8X,' UPPER')
1001 FORMAT(1X,1H*,2X,A,2X,1H*)
1002 FORMAT(1X,1H*,76X,1H*/1X,78(1H*))
1004 FORMAT(7(2X,A8))
1005 FORMAT(7F10.0)
1006 FORMAT(7I10)
1007 FORMAT(/5X,'OBSERVED DATA'/1X,13(1H=)/1X,'OBS. NO.',5X,
1 'TIME ',9X,' CONC ')  
1008 FORMAT(5X,A,4(1H.),F12.4,I9,2(2X,F12.4))
1009 FORMAT(/1X,'OBSERVED DATA'/1X,13(1H=)/1X,'OBS. NO.',5X,
1 ' TIME ',9X,' CONC ')
1010 FORMAT(1X,I5,6X,F12.4,4X,F12.4)
1011 FORMAT(/1X,'ITERATION',6X,'SSQ',4X,5(5X,A))
1012 FORMAT(1X,I5,3X,D13.3,2X,7(F13.4))
1013 FORMAT(/1X,'CORRELATION MATRIX'/1X,18(1H=)/4X,10(4X,I2,5X))
1014 FORMAT(1X,I3,10(2X,F7.4,2X))
1015 FORMAT(/1X,'NON-LINEAR LEAST SQUARES ANALYSIS, FINAL RESULTS'
1/1X,48(1H=)/62X,'95% CONFIDENCE LIMITS'/1X,'VARIABLE',4X,'NAME'
2,8X,'VALUE',8X,'S.E.COEFF.',3X,'T-VALUE',5X,'LOWER',10X,'UPPER')
1016 FORMAT(4X,I2,4X,A,1X,F13.4,3X,F13.4,2X,F8.2,1X,F13.4,2X,F13.4)
1017 FORMAT(//10X,8(1H-),'OBSERVED AND FITTED RESULTS',8(1H-)/
159X,'REST=',/5X,'NO',8X,'TIME',10X,'OBS',11X,'FITTED',10X,'DUAL')
1018 FORMAT(5X,I2,A1,1X,F10.3,1X,3(A1,F9.4))
1020 FORMAT(//1X,'END OF PROBLEM'//1X,14(1H=/)
1030 FORMAT(//1X,9(1H-),'RESULTS FOR INITIAL COEFFICIENT VALUES',9(1H-)
11X,'NO',10X,'TIME',10X,'CONC.'
1033 FORMAT(1X,I2,3X,2(A1,F12.4))
1034 FORMAT(1X,'CONVERGENCE CRITERIA NOT MET IN',I3,' ITERATIONS')
1036 FORMAT(//5X,'INPUT PARAMETERS'/5X,16(1H-)/5X,'NN=',T11,10X,'NSTEP
1S='/,I7,10X,'DELX=',F9.4/5X,'DELT=',F9.4,10X,'TP=',F11.4,10X,'CI=',
2F11.4/5X,'C0=',F11.4,10X,'CT=',F11.4,10X,'TOL=',F10.4)
1038 FORMAT(//1X,'NO FURTHER DECREASE IN SSQ OBTAINED AFTER ',I2,' TRIA
1LS')
1041 FORMAT(//1X,'RSQUARE FOR REGRESSION =',F10.8)
1042 FORMAT(1X,'NON-LINEAR LEAST SQUARES ANALYSIS, FINAL RESULTS'
1/1X,48(1H=)//54X,'95% CONFIDENCE LIMITS'/1X,'VARIABLE',4X,'NAME'
2,8X,'VALUE','6X','S.E.COEFF.','7X','LOWER','10X','UPPER')
1043 FORMAT(1X,I2,6X,A,1X,F13.4,3X,1F13.4,1X,F13.4,2X,1F13.4)
1047 FORMAT(4(F15.4),I3)
1050 FORMAT('Run Time was ... ',I8, ' seconds')
1210 FORMAT(F12.4,A1,F12.4)
C
C FUNCTION SLOPE(MODE,AK,ST,CT,C1)
C
C PURPOSE: TO EVALUATE SLOPE OF THE ISOTHERM S(C)
C
---
CGCR
IF(MODE.EQ.1) THEN
    --- LINEAR PARTITIONING -----
C    AK = EQUILIBRIUM PARTITIONING COEFFICIENT
    SLOPE = AK
    RETURN
ELSIF(MODE.EQ.2) THEN
    --- LANGMUIR PARTITIONING -----
C    SLOPE = ST*AK/(ST+C1)**2
    RETURN
ELSIF(MODE.EQ.3) THEN
    --- FREUNDLICH PARTITIONING -----
C    SLOPE = ST*AK*(C1**(ST-1.0))
CGCR
RETURN
ENDIF
END
Appendix D

BIOPLUME II v1.1 Code

The 2-dimensional horizontal transport model BIOPLUME II developed by Rifai, et al. (1987) has been modified to include a variable source input. A brief description of the modified model and its use is given here.

BIOPLUME II v1.0 Modifications

The modifications to BIOPLUME II v1.0 include changes to the main program MAIN, changes to four of the subroutines, a change to the include file params, and the addition of a subroutine. Changes were made to subroutines PARLOD, VELO, MOVE, and CHMOT. The additional subroutine is called ASMOD. These subroutines are highlighted on the attached subroutine call diagram, figure D.1. A further description of each of these modifications is as follows:

1. MAIN

a. An output file called CNRECH is opened. This file will store the variables TAU(ZX,ZY) and CNRECH(ZX,ZY) every time the subroutine ASMOD is called. However, it will only store these variables for the first cell encountered with a residual source. The purpose of this is to provide a means of observing the change in residual source concentration versus pore volumes flushed. Additionally,
the values are separated by a tab so that the file can easily be imported into a graphics package such as CricketGraph.

b. If a residual source is present, the subroutine VERO is called for at every time step. This is to insure that the number of particle moves within a given time step is adequate to simulate the residual source loading.

2. params

An additional parameter NCP is specified here. This value is the maximum number of components that can be included in the model.

3. PARLOD

a. Initialize control variables RSMASS and RSCMPS.
b. Initialize matrices EOM, TAU, and MLT.
c. Initialize vectors CWI, CWL, THETA0, THETAW, ASG, and ASD.
d. For each code ID, read the additional variables RSFLAG, RSEOM, RSMLT, and RSDLTC.
e. For the first residual source code ID encountered: Set DLTC equal to RSDLTC, RSCMPS equal to RSFLAG, and read the individual component variables. These operations are only done for the first residual source code ID
encountered, therefore subsequent values for RSFLAG and RSDLTC will be read but not used.

f. Adjust the recharge rate variable RECH by dividing by the factor RSMLT. In addition, adjust the recharge concentration CNRECH by multiplying by the factor RSMLT. The purpose of this operation is to provide a means of dampening the effects of unrealistic hydraulic mounds which may be created by relatively high recharge rates.

g. Set the variable EOM(ZX,ZY) equal to RSEOM for each cell with a node ID which corresponds to the current code ID. Similarly set MLT(ZX,ZY) equal to RSMLT.

h. Write the variables associated with the residual source to the output file.

4. VELO

a. If a residual source is present, then proceed with the following to determine the minimum number of particle moves necessary to adequately model the residual source.

b. Outermost loop: Determine if a residual source is present for each cell. If not check the next cell, if so proceed with the following.

c. Adjust the recharge rate to its true value.

d. First interior loop: The particle move time step will be set equal to the total time step divided by the number of
particle moves. The number of particle moves will start with one and will be incremented by one as necessary.

e. Second interior loop: Check each interval within the time step to determine if the number of particle moves specified is adequate. This is done by determining what the average value of the residual source leachate concentration, CNRECH, would be for each interval and comparing this to what CNRECH should be at the beginning of the interval and at the end of the interval. If the error is greater than the specified criteria DLTC, then the number of particle moves required is incremented by one and the procedure continues from there (at the first interior loop). However, if the error is within the specified criteria, then the next interval within the time step is checked similarly. When all intervals meet the criteria, the required number of moves is saved as the variable MI.

f. When the procedure has been completed for each cell, the maximum particle move time step (as determined by the minimum number of moves required) is compared to the maximum particle move time step determined by the other stability criteria. The lesser of these values becomes the limiting criteria.
5. **MOVE**

The subroutine ASMOD is called if a residual source is present.

6. **CHMOT**

The cumulative mass pumped in by a residual source is printed to the output file.

7. **ASMOD**

   a. Determine if a residual source is present for each cell. If not check the next cell, if so proceed with the following.
   
   b. Determine the mass leached at the beginning and at the end of the time interval for each component. Sum the change in mass leached for all components.

   c. Determine the new value for the variable CNRECH(ZX,ZY).

   d. Proceed with the next cell.
Figure D.1  Subroutine Call Diagram for BIOPLUME II v1.1
**Modified Input Data Set for BIOPLUME II v1.1**

There are ten new variables in the modified version of BIOPLUME II. Four variables have been added to the original card #7. These variables follow the six original variables in the order: RSCMPS, EOM, MLT, and DLTC. When a residual source is to be simulated, and RSCMPS > 0, then an additional card with six variables is read. This card is read for each component, but only once in a single simulation. These variables are input in the order: CWI, CWL, THETA0, THETA0W, ASG, and ASD. The ten new variables are defined as follows. Note that the dimensions ZX and ZY are the number of cells in the model grid in the X and Y directions, respectively, and the dimension NCP is the maximum number of components which can be included.

**Variable** | **Description**
--- | ---
RSCMPS | Number of residual oil components
EOM(ZX,ZY) | Thickness of the residual oil zone
MLT(ZX,ZY) | Factor for adjusting hydraulic conditions
DLTC | Criteria for determining maximum time step
CWI(NCP) | Initial plateau concentration in the water phase
CWL(NCP) | Final plateau concentration in the water phase
THETA0(NCP) | Bulk oil volume
THETA0W(NCP) | Bulk water volume
ASG(NCP) | Fitted coefficient
ASD(NCP) | Fitted exponent

An example data set is shown in figure D.2. This example is for the simulation of the transport of a single component. The new variables are shown in bold.
Test Case - Toluene
4 1 10 15 9 300 1 7 0 200 0 9 2 0 0 0 0 0 1
4 0 .001 .356 10. 0 0 0 300.0 200.0 .25 .5 .75
0 0 0 0 0
0 .015
0 20.
0 0
1 1
0,0,0,0,0,0,0,0,0,0,0,0,0,0,0
0,3,3,3,3,3,3,3,3,3,3,3,3,0
0,0,0,0,0,0,0,0,0,0,0,0,0,0
0,0,0,0,0,0,0,0,0,0,0,0,0,0
0,0,0,0,0,0,0,0,0,0,0,0,0,0
0,0,0,0,0,0,0,0,0,0,0,0,0,0
0,0,0,0,0,0,0,0,0,0,0,0,0,0
0,0,0,0,0,0,0,0,0,0,0,0,0,0
0,0,0,0,0,0,0,0,0,0,0,0,0,0
0,0,0,0,0,0,0,0,0,0,0,0,0,0
0,0,0,0,0,0,0,0,0,0,0,0,0,0
0,0,0,0,0,0,0,0,0,0,0,0,0,0
0,0,0,0,0,0,0,0,0,0,0,0,0,0
0,0,0,0,0,0,0,0,0,0,0,0,0,0
0,0,0,0,0,0,0,0,0,0,0,0,0,0
1,0.23,0,-.000000085,1,1,.5,10,.3
40.73,.067,.048,.308,.2044,.80
3,1,0,false,0,0,0,0,1,0
1 1
0 0 0 0 0 0 0 0 0 0 0 0 0 0
0 100 100 100 100 100 100 100 100 100 100 100 0
0 100 100 100 100 100 100 100 100 100 100 100 0
0 100 100 100 100 100 100 100 100 100 100 100 0
0 100 100 100 100 100 100 100 100 100 100 100 0
0 100 100 100 100 100 100 100 100 100 100 100 0
0 100 100 100 100 100 100 100 100 100 100 100 0
0 100 100 100 100 100 100 100 100 100 100 100 0
0 100 100 100 100 100 100 100 100 100 100 100 0
0 100 100 100 100 100 100 100 100 100 100 100 0
0 90 90 90 90 90 90 90 90 90 90 90 0
0 0 0 0 0 0 0 0 0 0 0 0 0
0 0

Figure D.2 Example data set for the modified BIOPLUME II v1.1
Use of the Modified Model BIOPLUME II v1.1

The use of the modified model is identical to the use of the original model. The use of the original model, BIOPLUME II v1.0, is described in detail by Rifai, et al. (1987).
Modified Program Listing

Only the modified program code is included here. Code modifications are preceded and followed by the comment line CGCR.

The subroutines not included here can be obtained from:

Dept. of Envir. Science & Engr.
Rice University
P. O. Box 1892
Houston, TX  77251

MAIN

******************************************************************************
* *
*  Downloaded from IBM mainframe 1/11/88  
  John Haasbeek  
* *
*  Note:  SAVE statements have been added to the beginning  
  of all subroutines.  
* *
*  Unit 6 is now unit 2.  Unit 5 is unit 1.  
* *
******************************************************************************
* *
*  BIOPLUME II  
*  VERSION 1.1  
*  PROGRAMMED BY HANADI S. RIFAI, JUNE 1987  
*  MODIFIED BY GEORGE C. ROBINSON, JANUARY 1991  
*  RICE UNIVERSITY  
*  BASED ON  
* *
*  SOLUTE TRANSPORT AND DISPERSION IN A POROUS MEDIUM  
*  NUMERICAL SOLUTION --- METHOD OF CHARACTERISTICS  
*  PROGRAMMED BY J. D. BREDEHOEFT AND L. F. KONIKOW  
*    REVISED APRIL 1979, MARCH 1980  
*    REVISED DECEMBER 1980  
*    REVISED AUGUST 1981, JUNE 1982  
*    REVISED OCTOBER 1983  
*  REV. JUNE-AUG. 1984 BY W. SANFORD TO ALLOW 16 PTS. PER NODE  
*  REV. MAY-AUG. 1985 BY L. KONIKOW AND M. PERSON TO INCLUDE:  
*    DECAY AND EQUILIBRIUM SORPTION-DESORPTION REACTIONS  
* *
*  REV. JULY-DEC.1985 TO ALLOW SECONDARY SUBGRID FOR TRANSPORT  
* *
*
include params

DOUBLE PRECISION DMIN1, DEXP, DLOG, DABS
REAL *8TMRX, VPRM, HI, HR, HC, HK, WT, REC, RECH, TIM, AOPT, TITLE
REAL *8XDEL, YDEL, S, AREA, SUMT, RHO, PARAM, TEST, TOL, PINT, HMIN, PYR
REAL *8TSUM, ANTIM, TDEL
REAL *8TINT, ALPHAI, ANITP

REAL *8CWI, CWL, THETAO, THETAW, ASG, ASD, EOM, TAU, MLT, RSMASS, DLTC

LOGICAL BIODEG

COMMON /PRMJ/ NTIM, NPMT, NPNT, NITP, N, NX, NY, NP, NREC, INT, NNX, NNY, NUMO
1BS, NMOV, IMOV, NPMAX, ITMAX, N2CRIT, IPRNT, NPTPND, NPNMV, NPNVL, NPNVD, N
2NCHV, NPDLC, ICHK
COMMON /PRMJ/ NP1, IPRNT1
COMMON /PRMC/ NODEID (ZX, ZY), NPCELL (ZX, ZY), NPOLD (ZX, ZY), LIMBO (500),
1IXOBS (5), IYOBS (5)
COMMON /HEDA/ THCK (ZX, ZY), PERM (ZX, ZY), TMWL (5, 50), TMOBS (50), ANFCTR
COMMON /HEDB/ TMRX (ZX, ZY, 2), VPRM (ZX, ZY), HI (ZX, ZY), HR (ZX, ZY), HC (ZX,
1ZY), HK (ZX, ZY), WT (ZX, ZY), REC (ZX, ZY), RECH (ZX, ZY), TIM (100), AOPT (20),
2TITLE (10), XDEL, YDEL, S, AREA, SUMT, RHO, PARAM, TEST, TOL, PINT, HMIN, PYR
COMMON /HEDC/ MX, MY, MMX, MMY, NMX, NMY, MCHK
COMMON /CHMA/ PART (3, ZP), CONC (ZX, ZY), TMCN (5, 50), VX (ZX, ZY), VY (ZX
1, ZY), CONINT (ZX, ZY), CNRECH (ZX, ZY), POROS, SUMICH, BETA, TIMV, STORM,
2MI, CMSIN, CMSOUT, FLMIN, FLMOT, SUMIO, CELDIS, DLTRAT, CSTM
COMMON /CHMA1/ PART1 (3, ZP), CONC1 (ZX, ZY), TMCN1 (5, 50), CONTNO (ZX, ZY
1), CNREC (ZX, ZY), STORM1, STOMIO, CMSIN1, CMSOUT1, FLMIN1, FLMOT1, SUMIO1,
2CSTORO

COMMON /RSRC/ CWI (NCP), CWL (NCP), THETAO (NCP), THETAW (NCP), ASG (NCP)
1, ASD (NCP), EOM (ZX, ZY), TAU (ZX, ZY), MLT (ZX, ZY), RSCMPS, RSMASS, DLTC

COMMON /JFPH/ BIODEG

INTEGER*4-toolbox
INTEGER*4 ERASERECT
INTEGER*4 MOVETO
INTEGER*4 SYSBEEF
parameter(SYSBEEF=Z'9C808000')
PARAMETER(ERASERECT=Z'8A330000')
PARAMETER(MOVETO=Z'89309000')
INTEGER*2 rect (4)
integer*4 timel, time2

INTEGER RSCMPS

character*64 infil, outfIl
c.... Files
c        call getfil('TEXT',infil)
        if (infil.eq.' ') stop
        call putfil('TEXT',outfil,infil)
        if (outfil.eq.' ') stop
        call TIME(timel)

CGCR
        OPEN (15,FILE='CNRECH',STATUS='NEW')
CGCR
C
C          **********************************************
C          ---LOAD DATA---
C          INT=0
C          TMSUM=0.0
C
CJFH
        CALL TOOLBX(MOVETO,10,15)
        WRITE(*,*) 'Loading Data ...'
CJFH
        CALL PARLOD
        CALL TOOLBX(MOVETO,10,15)
        WRITE(*,'(1X,10A8)') TITLE
        WRITE(*,*)
        WRITE(*,*) 'Number of Pumping Periods ... ',NPMP
        WRITE(*,*) 'Number of Time Steps ... ',NTIM
CJFH
        WRITE(3,*) 'Biopluce II'
        WRITE(3,'(3I5)') NX,NY,NTIM
        IF (BIODEG) THEN
            WRITE(3,*) 1
        ELSE
            WRITE(3,*) 0
        END IF
CJFH
        CALL GENPT
        CALL GENPT1
C
C          **********************************************
C          ---START COMPUTATIONS---
C
C          ---COMPUTE ONE PUMPING PERIOD---
C          DO 150 INT=1,NPMP
C          IF (INT.GT.1) TMSUM=TMSUM+PYR
C          IF (INT.GT.1) CALL PARLOD
C          IPCK=0
C          DO 130 N=1,NTIM
C          IPRNT=0
C          IPRNT1=0
C
C          ---LOAD NEW DELTA T---
C          TINT=SUNT-TMSUM
C          TDEL=DMINI(TIM(N),PYR-TINT)
C          SUMT=SUNT+TDEL
C          IF (TDEL.EQ.(PYR-TINT)) IPCK=1
C          TIM(N)=TDEL
C          RENN=MOD(N,NPNT)
C
C          **********************************************
IF (S.EQ.0.0.AND.ICHK.EQ.0.AND.(N.GT.1.OR.INT.GT.1)) GO TO 101

CJFH Write Status info to screen in proper position
CJFH
rect(1) = 50
rect(2) = 0
rect(3) = 500
rect(4) = 600
call toolbx(ERASERECT,rect)
call toolbx(MOVETO,10,60)
WRITE(*,*) 'Computing Heads for Pumping Period ... ',INT
call toolbx(MOVETO,10,75)
WRITE(*,*) ' Time step ... ',N
CALL ITERAT

CJFH IF (REMN.EQ.0.0.OR.N.EQ.NTIM.OR.IPCK.EQ.1) CALL OUTPT
CALL VEO

CGCR
101 IF (S.EQ.0.0.AND.ICHK.EQ.0.AND.(N.GT.1.OR.INT.GT.1)
1 .AND.(RSCMPS.GT.0)) CALL VELO

CGCR
CALL MOVE

C **********************************************************************
C ---STORE OBS. WELL DATA FOR TRANSIENT FLOW PROBLEMS---
C IF (S.EQ.0.0) GO TO 120
IF (NUMOBS.LE.0) GO TO 120
J=MOD(N,50)
IF (J.EQ.0) J=50
TMOBS(J)=SUMT
DO 110 I=1,NUMOBS
TMWL(I,J)=HK(IXOBS(I),IYOBS(I))
IX=IXOBS(I)-MX+1
IF (IXOBS(I).LT.MX.OR.IXOBS(I).GT.MMX) GO TO 110
IY=IYOBS(I)-MY+1
IF (IYOBS(I).LT.MY.OR.IYOBS(I).GT.MMY) GO TO 110
TMCN(I,J)=CONC(IX,IY)
TMCN1(I,J)=CONC1(IX,IY)
110 CONTINUE
C **********************************************************************
C ---OUTPUT ROUTINES---
C 120 IF (REMN.EQ.0.0.OR.N.EQ.NTIM.OR.MOD(N,50).EQ.0.OR.IPCK.EQ.1)
1 CALL CHMT

CJFH IF (BIODEG) THEN
END IF
CJFH IF (SUMT.GE.(PYR+TMSUM)) GO TO 140

130 CONTINUE

C **********************************************************************
C ---SUMMARY OUTPUT---
C 140 CONTINUE
IPRNT=1
IPRNT1=1
CALL CHMT
CJFH
   IF (BIODEG) CALL CHMOT1
CJFH
   150 CONTINUE
C
   **********************************************************************
   IF (NPNCBV.EQ.0) GO TO 155
   **********************************************************************
   CONTINUE
C
   close(1)
close(2)
close(3)
call TIME(time2)
write(*,*)
write(*,*)
call toolbx(SYSBEEP,5)
call toolbx(SYSBEEP,5)
write(*,*) 'Comutations Finished'
write(*,*) 'Run time was   ... ',time2-time1,' seconds'
write(*,*)
pause 'Hit return to continue ...'
END
params

IMPLICIT INTEGER*4 (I-N)

INTEGER 2X, 2Y, 2Z, 2P, NCP

PARAMETER(2X = 22)
PARAMETER(2Y = 22)
PARAMETER(2Z = 22)
PARAMETER(2P = 9300)
PARAMETER(NCP = 5)
PARLOD

SUBROUTINE PARLOD

include params

DOUBLE PRECISION DMINI, DEXP, DLOG, DABS
REAL *8 TMXR, VRPM, HI, HR, HC, HK, WT, REC, RECH, TIM, AOPT, TITLE
REAL *8 XDEL, YDEL, S, AREA, SUMT, RHO, PARAM, TEST, TOL, PINT, HMIN, PYR
REAL *8 FCTR, TIMX, TINIT, DIES, YNS, XNS, RAT, HMX, HMY
REAL *8 TSMUX, TSMUY, TDEL
REAL *8 DXINV, DXINV, ARINV, P0RINV
REAL *8 TINT, ALFAHAL, ANITP

INTEGER OVERRD, RSCMPS, RFLAG, ICNT

LOGICAL BIODEG

COMMON /PRMJ/ NTIM, NPME, NPNT, NITP, N, NX, NY, NP, NREC, INT, NNX, NNY, NUMO
1BS, NMOV, IMOV, NPMAX, ITMCR, IPRNT, NPTPND, NPTMNV, NPTVNL, NPTND, N
2PNCHV, NPDEL, ICHK
COMMON /PRMJ1/ NP1, IPRNT1
COMMON /PRMC/ NODEID (2X, YZ), NPCELL (2X, YZ), NPOLD (2X, YZ), LIMBO (500),
1XOB5 (5), YOB5 (5)
COMMON /PRMC1/ NPCELO (2X, YZ), NPOLD1 (2X, YZ), LIMBO1 (500)
COMMON /HDFA/ THCK (2X, YZ), PERM (2X, YZ), TMWL (5, 50), TMOB5 (50), ANFCTR
COMMON /HDFB/ TMXR (2X, YZ), VRPM (2X, YZ), HI (2X, YZ), HR (2X, YZ), HC (2X,
1Y), HK (2X, YZ), WT (2X, YZ), REC (2X, YZ), RECH (2X, YZ), TIM (100), AOPT (20),
2TITL (10), XDEL, YDEL, S, AREA, SUMT, RHO, PARAM, TEST, TOL, PINT, HMIN, PYR
COMMON /HDFC/ MX, MY, MMX, MMY, NMX, NMY, MCHK
COMMON /CHMA/ PART (3, ZP), CONC (2X, YZ), TMCN (5, 50), VX (2X, YZ), VY (2X
1, YZ), CONINT (2X, YZ), CNRECH (2X, YZ), POROS, SUMICH, BETA, TIMV, STORM, STOR
2M1, CMSKJ, CMSOUT, FLM1, FLMOT, SUMC1, CMSOU1, CMSO1, FLM11, FLMOT1, SUMO1,
2STORO
COMMON /CHMR/ RF, DK, RHOB, THALF, DECAY, ADSORB, SORB, DMAS 1, CSTM2
COMMON /CHMR1/ CSTM2
COMMON /DCAS/ DEC1, DEC2, DECY, DMASS2, DMASS3
COMMON /BALM/ TOTL, TOTI, TPN, TOUT
COMMON /XINV/ DXINV, DXINV, ARINV, P0RINV
COMMON /CHMAC/ SUMC (2X, YZ), VXYDY (2X, YZ), VYBDY (2X, YZ)
COMMON /CHMC1/ SUMC1 (2X, YZ)

COMMON /RSRC/ CWI (NCP), CNL (NCP), THETAO (NCP), THETAW (NCP), ASG (NCP)
1, ASD (NCP), EOM (2X, YZ), TAU (2X, YZ), MLT (2X, YZ), RSCMPS, RSM, DLTC

COMMON /JFJ/ BIODEG

**************************************************************************************************
SAVE

CJFH
IF (INT.GT.1) GO TO 10
WRITE (2,749)
WRITE (2,750)
READ (1,720) TITLE
WRITE (2,730) TITLE
C
******************************************************************************
C
---INITIALIZE TEST AND CONTROL VARIABLES---
STORMI=0.0
STOMIO=0.0
SCORBI=0
RHOB=0.0
TEST=0.0
TCTLQ=0.0
TCTLQI=0.0
TPIN=0.0
TPOUT=0.0
SUMT=0.0
SUMTCH=0.0
INT=0
IPRNT=0
IPRNTI=0
MX=1
MY=1
MCHK=0
NCA2=0
NCA=0
N=0
IMOV=0
NMOV=0
ICHK=0
DMASS1=0.0
DMASS2=0.0
DMASS3=0.0
RF=1.0
DECAY=0.0
THALF=0.0
DEC1=0.0
DEC2=0.0
CGCR
RSMASS = 0.0
RSCMPS = 0
CGCR
CJFH
BIODEG = .FALSE.
CJFH
******************************************************************************
C
---LOAD CONTROL PARAMETERS---
READ (1,*) NTIM,NPMP,NX,NY,NPMAX,NPNT,NITP,NUMOBS,ITMAX,NREC,NPT
1PND,NCODES,NPNTMV,NPNTVL,NPNTD,NPDEL,C,NPNCVH,NREACT
NMX=NX
NMY=NY
MMX=NX-1
MMY=NY-1
C
---READ UPPER LEFT AND LOWER RIGHT NODAL COORDS. OF
C TRANSPORT SUBGRID, IN FREE FORMAT, IF NX.LT.0---
IF (NX.GT.0) GO TO 5
NX=-NX
MCHK=1
READ (1,*) MX,MY,MMX,MMY
NMX=MMX-NX+1
NNY=MMY-MY+1
5 CONTINUE
READ (1,*) PINT,TOL,POROS,BETA,S,TIMX,TINIT,XDEL,YDEL,DLTRAT,CEL
IDIS,ANFCTR
C --READ REACTION TERMS IN FREE FORMAT--
IF (NREACT.EQ.1) READ (1,*) DK,RHOB,THALF,DEC1,DEC2
NX=-NX-1
NNY=NNY-1
NP=NPMAX
NP1=NPMAX
DXINV=1.0/XDEL
DYINV=1.0/YDEL
ARINV=DXINV*DYINV
PORINV=1.0/POROS
RF=1.0+((DK*RHOB)/POROS)
IF (THALF.GT.0.0) DECAY=ALOG(2.0)/THALF
DECY = DEC1+DEC2
C ---PRINT CONTROL PARAMETERS---
WRITE (2,755)
WRITE (2,760)
WRITE (2,770) NX,NX,XDEL,YDEL
IF (MCHK.GT.0) WRITE (2,775) NX,NX,MY,MMX,MMY
WRITE (2,780) NTIM,NPMP,PINT,TIMX,TINIT
WRITE (2,790) S,POROS,BETA,DLTRAT,ANFCTR
WRITE (2,870) NITP,TOL,ITMAX,CELDIS,NPMAK,NPTPD
IF (NPTPD.NE.4 .AND. NPTPD.NE.5 .AND. NPTPD.NE.8 .AND. NPTPD.NE.9 .AND. NPTPD.NE.16 .AND. NPTPD.NE.1) WRITE (2,880)
IF (NPTPD.EQ.1) WRITE (2,882)
IF (NITP.LE.0) WRITE (2,885)
WRITE (2,888)
WRITE (2,890) NPNT,NPNTMV,NPNTVL,NPNTD,NUMBS,NREC,NCODES,NFNCBV,NPDEL
WRITE (2,895) DK,RHOB,RF,THALF,DECAY
WRITE (2,896) DEC1,DEC2
GO TO 20
C *************************************************
C ---READ DATA TO REVISE TIME STEPS AND STRESSES FOR SUBSEQUENT
C PUMPING PERIODS---
C 10 READ (1,*) ICHK
IF (ICHK.LE.0) WRITE (2,1110) INT
IF (ICHK.LE.0) GO TO 20
READ (1,*) NTIM,NPNT,NITP,ITMAX,NREC,NPNTMV,NPNTVL,NPNTD,NPDEL
1,NPNCBV,PINT,TIMX,TINIT
WRITE (2,1080) INT
WRITE (2,1090) NTIM,NPNT,NITP,ITMAX,NREC,NPNTMV,NPNTVL,NPNTD,NPDEL
1C,NPNCBV,PINT,TIMX,TINIT
C *************************************************
C ---LIST TIME INCREMENTS---
C 20 DO 30 J=1,100
TIM(J)=0.0
30 CONTINUE
PYR=PINT*86400.0*365.25
TIM(1)=TINIT
IF (NPNTMV.EQ.0) NPNTMV=999
IF (S.EQ.0.0) GO TO 50
DO 40 K=2,NTIM
40 TIM(K)=TIMX*TIM(K-1)
WRITE(2,470)
WRITE(2,490) TIM
IF (TINIT.GT.PYR) WRITE(2,475)
GO TO 60
50 NTIM=1,NTIM
DO 55 K=1,NTIM
55 TIM(K)=PYR/NTIM
WRITE(2,480) TIM(1)
C**************************************************************************
C     ---INITIALIZE MATRICES---
160 IF (INT.GT.1) GO TO 100
DO 70 IY=1,NY
DO 70 IX=1,NX
VPRM(IX,IY)=0.0
PERM(IX,IY)=0.0
CGCR
EOM(IX,IY) = 0.0
TAU(IX,IY) = 0.0
MLT(IX,IY) = 0.0
CGCR
THCK(IX,IY)=0.0
REC(IX,IY)=0.0
REC(IX,IY)=0.0
NODEID(IX,IY)=0
TMRX(IX,IY,1)=0.0
TMRX(IX,IY,2)=0.0
HI(IX,IY)=0.0
HR(IX,IY)=0.0
HC(IX,IY)=0.0
HK(IX,IY)=0.0
WT(IX,IY)=0.0
VX(IX,IY)=0.0
VY(IX,IY)=0.0
VXBDY(IX,IY)=0.0
VYBDY(IX,IY)=0.0
70 CONTINUE
CGCR
DO 72 JC=1,NCP
CWI(JC) = 0.0
CWL(JC) = 0.0
THETAG(JC) = 0.0
THETAW(JC) = 0.0
ASG(JC) = 0.0
ASD(JC) = 0.0
72 CONTINUE
CGCR
DO 75 IY=1,NMY
DO 75 IX=1,NMX
CNRECH(IX,IY)=0.0
CNRECO (IX, IY) = 0.00
CONC (IX, IY) = 0.0
CONC1 (IX, IY) = 0.0
CONTNT (IX, IY) = 0.0
CONTNO (IX, IY) = 0.0
SUMC (IX, IY) = 0.0
SUMC1 (IX, IY) = 0.0
NPCELL (IX, IY) = 0
NPCelo (IX, IY) = 0
75 CONTINUE

C

******************************************************************************
C

---READ OBSERVATION WELL LOCATIONS---

IF (NUMOBS .LE. 0) GO TO 100
WRITE (2, 755)
WRITE (2, 900)
DO 80 J = 1, NUMOBS
READ (1, *) IX, IY
WRITE (2, *) J, IX, IY
IXOBS (J) = IX
IYOBS (J) = IY
DO 90 I = 1, NUMOBS
DO 90 J = 1, 50
TMWL (I, J) = 0.0
TMCN1 (I, J) = 0.0
90 TMCN (I, J) = 0.0

C

******************************************************************************
C

---READ PUMPAGE DATA -- (X-Y COORDINATES AND RATE IN CFS)---

---SIGNS : WITHDRAWAL = POS.; INJECTION = NEG.---
C

---IF INJ. WELL, ALSO READ CONCENTRATION OF INJECTED WATER---
C

---IF O2 INJ. WELL, READ CONC OF OXYGENATED WATER---

100 IF (NREC .LE. 0) GO TO 120
IF (INT.GT.1 .AND. ICHK .LE. 0) RETURN
WRITE (2, 755)
WRITE (2, 910)
DO 110 I = 1, NREC
READ (1, *) IX, IY, FCTR, CNREC, CNREC1
CJPH
IF (CNREC1 .NE. 0.0) BIODEG = .TRUE.
CJPH
JX = IX - MX + 1
JY = IY - MY + 1
IF (JX .LT. 1.0 .OR. JY .LT. 1.0 .OR. JX .GT. NMX .OR. JY .GT. NMY) GO TO 105
IF (FCTR .LT. 0.0) CNRECH (JX, JY) = CNREC
IF (FCTR .GT. 0.0) CNRECO (JX, JY) = CNREC1
105 REC (IX, IY) = FCTR
110 WRITE (2, 821) IX, IY, REC (IX, IY), CNREC, CNREC1
C

******************************************************************************
C

120 IF (INT .GT. 1) RETURN
AREA = XDEL * YDEL
WRITE (2, 755)
WRITE (2, 690) AREA
WRITE (2, 600)
WRITE (2, 610) XDEL
WRITE (2, 610) YDEL

C

******************************************************************************
C

---READ TRANSMISSIVITY IN FT**2/SEC INTO VPRM ARRAY---
C ---FCTR = TRANSMISSIVITY MULTIPLIER ---> FT**2/SEC---
WRITE(2,530)
WRITE(2,755)
READ (1,*) INPUT,FCTR
DO 160 IY=1,NY
IF (INPUT.EQ.1) READ (1,*) (VPRM(IX,IY),IX=1,NX)
DO 150 IX=1,NX
IF (INPUT.NE.1) GO TO 130
VPRM(IX,IY)=VPRM(IX,IY)*FCTR
GO TO 140
130 VPRM(IX,IY)=FCTR
140 IF (IX.EQ.1.OR.IX.EQ.NX) VPRM(IX,IY)=0.0
IF (IY.EQ.1.OR.IY.EQ.NY) VPRM(IX,IY)=0.0
150 CONTINUE
160 WRITE(2,840) (VPRM(IX,IY),IX=1,NX)
C *******************************************************************************
C ---SET UP COEFFICIENT MATRIX --- BLOCK-CENTERED GRID---
C ---AVERAGE TRANSMISSIVITY --- HARMONIC MEAN---
C IF (ANFCTR.NE.0.0) GO TO 170
WRITE(2,1050)
ANFCTR=1.0
170 PIES=3.1415927*3.1415927/2.0
YNS=YNY
XNS=NXNX
HMIN=2.0
DO 180 IY=2,NNY
DO 180 IX=2,NNX
IF (VPRM(IX,IY).EQ.0.0) GO TO 180
TMRX(IX,IY,1)=2.0*VPRM(IX,IY)*VPRM(IX+1,IY)/(VPRM(IX,IY)*XDEL+VPRM
1(IX+1,IY)*XDEL)
TMRX(IX,IY,2)=2.0*VPRM(IX,IY)*VPRM(IX,IY+1)/(VPRM(IX,IY)*YDEL+VPRM
1(IX,Y+1)*YDEL)
C ---ADJUST COEFFICIENT FOR ANISOTROPY---
TMRX(IX,IY,2)=TMRX(IX,IY,2)*ANFCTR
C ---COMPUTE MINIMUM ITERATION PARAMETER (HMIN)---
IF (TMRX(IX,IY,1).EQ.0.0) GO TO 180
IF (TMRX(IX,IY,2).EQ.0.0) GO TO 180
RAT=TMRX(IX,IY,1)*YDEL/(TMRX(IX,IY,2)*XDEL)
HMX=PIES/(YNS*(1.0+RAT))
HMY=PIES/(YNS*(1.0+1.0/RAT))
IF (HMX.LT.HMIN) HMIN=HMX
IF (HMY.LT.HMIN) HMIN=HMY
180 CONTINUE
IF (NX.GT.3.AND.NY.GT.3) GO TO 185
HMX=PIES/XNS
HMY=PIES/YNS
HMIN=DMIN1(HMIN,HMX,HMY)
185 CONTINUE
C *******************************************************************************
C ---READ AQUIFER THICKNESS---
WRITE(2,510)
WRITE(2,755)
READ (1,*) INPUT,FCTR
DO 210 IY=1,NY
IF (INPUT.EQ.1) READ (1,*) (THCK(IX,IY),IX=1,NX)
DO 200 IX=1,NX
IF (INPUT .NE. 1) GO TO 190
THCK(IX, IY) = THCK(IX, IY) * FCTR
GO TO 200
190 IF (VPRM(IX, IY) .NE. 0.0) THCK(IX, IY) = FCTR
200 CONTINUE
210 WRITE (2, 500) (THCK(IX, IY), IX = 1, NX)
C
C *****************************************************************************
C
C ---READ DIFFUSE RECHARGE AND DISCHARGE---
C
WRITE (2, 830)
WRITE (2, 755)
READ (1, *) INPUT, FCTR
DO 240 IY = 1, NY
IF (INPUT .EQ. 1) READ (1, *) (RECH(IX, IY), IX = 1, NX)
DO 230 IY = 1, NX
IF (INPUT .NE. 1) GO TO 220
RECH(IX, IY) = RECH(IX, IY) * FCTR
GO TO 230
220 IF (THCK(IX, IY) .NE. 0.0) RECH(IX, IY) = FCTR
230 CONTINUE
240 WRITE (2, 840) (RECH(IX, IY), IX = 1, NX)
C
C *****************************************************************************
C
C ---COMPUTE PERMEABILITY FROM TRANSMISSIVITY---
C
C ---COUNT NO. OF CELLS IN AQUIFER---
C
C ---SET NZCRIT = 2% OF THE NO. OF CELLS IN THE AQUIFER---
C
DO 250 IY = 1, NX
DO 250 IY = 1, NY
IF (THCK(IX, IY) .EQ. 0.0) GO TO 250
PERM(IX, IY) = VPRM(IX, IY) / THCK(IX, IY)
NCA = NCA + 1
IF (MCHK .EQ. 0) GO TO 250
IF (IX .LT. MX OR IX .GT. MMX) GO TO 250
IF (IX .LT. MY OR IX .GT. MMY) GO TO 250
NCA2 = NCA2 + 1
250 VPRM(IX, IY) = 0.0
C
AAQ = NCA * AREA
NZCRIT = (NCA + 25) / 50
IF (MCHK .GT. 0) NZCRIT = (NCA2 + 25) / 50
IF (NZCRIT .EQ. 0) NZCRIT = 1
WRITE (2, 620)
WRITE (2, 755)
DO 260 IY = 1, NY
260 WRITE (2, 840) (PERM(IX, IY), IX = 1, NX)
IF (MCHK .EQ. 0) GO TO 265
AAQ2 = NCA2 * AREA
WRITE (2, 633)
WRITE (2, 635) NCA, AAQ
WRITE (2, 634)
WRITE (2, 630) NCA2, AAQ2, NZCRIT
GO TO 267
265 CONTINUE
WRITE (2, 630) NCA, AAQ, NZCRIT
267 CONTINUE
C
C *****************************************************************************
C
C ---READ NODE IDENTIFICATION CARDS---
C
C ---SET VERT. PERM., SOURCE CONC., AND DIFFUSE RECHARGE---
---SPECIFY CODES TO FIT YOUR NEEDS---
WRITE(2,570)
READ (1,*) INPUT,FCTR
DO 280 IY=1,NY
IF (INPUT.EQ.1) READ (1,*), (NODEID(IX,IY), IX=1,NX)
DO 270 IX=1,NX
270 IF (INPUT.NE.1.AND.THCK(IX,IY).NE.0.0) NODEID(IX,IY)=FCTR
280 WRITE(2,580) (NODEID(IX,IY), IX=1,NX)
WRITE(2,920) NCODES
IF (NCODES.LE.0) GO TO 310
WRITE(2,930)

CGCR
ICNT = 1
DO 300 IJ=1,NCODES
READ (1,*) ICODE,FCTR1,FCTR2,FCTR4,FCTR3,OVERRD,RSFLAG,RSEOM,RSMLT
1 ,RSDLTC
IF (RSFLAG.GT.0 .AND. ICNT.EQ.1) THEN
DLTC = RSDLTC
RSCMPS = RSFLAG
DO 282 JC=1,RSCMPS
READ(1,*),CWJ(JC),CWI(JC),THETAO(JC),THETA(JC),THETAW(JC),ASG(JC),ASD(JC)
282 CONTINUE
ENDIF
CGCR
CJFH
IF (FCTR4 .NE. 0.0) BIODEG = .TRUE.
CJFH
DO 290 IX=1,NX
DO 290 IY=1,NY
IF (NODEID(IX,IY).NE.ICODE) GO TO 290
VPRM(IX,IY)=FCTR1
JX=IX-MX+1
JY=IY-MY+1
IF (JX.LT.1.OR.JY.LT.1.OR.JX.GT.NMX. OR.JY.GT.NMY) GO TO 285
CNRECH(JX,JY)=FCTR2
CNRECO(JX,JY)=FCTR4
285 CONTINUE
CGCR
IF (OVERRD.NE.0) THEN
RECH(JX,JY)=FCTR3 / RSMLT
CNRECH(JX,JY) = CNRECH(JX,JY) * RSMLT
ENDIF
IF (RSFLAG.NE.0) THEN
EOM(JX,JY) = RSEOM
MLT(JX,JY) = RSMLT
ENDIF
CGCR
290 CONTINUE
WRITE(2,860) ICODE,FCTR1,FCTR2,FCTR4
IF (OVERRD.NE.0) WRITE(2,1100) FCTR3
CGCR
IF (RSFLAG.GT.0) THEN
WRITE(2,1230)
WRITE(2,1240)
WRITE(2,1250) RSCMPS,RSEOM,RSMLT,DLTC
IF (ICNT .EQ. 1) THEN
WRITE(2,1210)
DO 295 IK=1,RSCMPS
     WRITE(2,1220) CWI(IK),CWL(IK),THETAO(IK),THETAW(IK)
        ,ASG(IK),ASD(IK)
295   CONTINUE
ENDIF
ENDIF
ICNT = ICNT + 1
300 CONTINUE

CGCR
310 WRITE(2,590)
     WRITE(2,755)
DO 320 IY=1, NY
320 WRITE(2,840) (VPRM(IX,IY),IX=1,NX)
C
     *******************************
     ---READ WATER-TABLE ELEVATION---
     WRITE(2,670)
     WRITE(2,755)
     READ (1,*)) INPUT,FCTR
     DO 350 IY=1, NY
     IF (INPUT.EQ.1) READ (1,*)) (WT(IX,IY),IX=1,NX)
     DO 340 IX=1, NX
     IF (INPUT.NE.1) GO TO 330
     WT(IX,IY)=WT(IX,IY)*FCTR
     GO TO 340
330 IF (THCK(IX,IY).NE.0.0) WT(IX,IY)=FCTR
     WRITE(2,680) (WT(IX,IY),IX=1,NX)
C
     ********************************
     ---SET INITIAL HEADS---
     DO 360 IX=1, NX
     DO 360 IY=1, NY
     HI(IX,IY)=WT(IX,IY)
     HC(IX,IY)=HI(IX,IY)
     HR(IX,IY)=HI(IX,IY)
360   HK(IX,IY)=HI(IX,IY)
C
     CALL OUTPT
C
     ****************************************
     ---COMPUTE ITERATION PARAMETERS---
     DO 370 ID=1,20
     AOPT(ID)=0.0
370   CONTINUE
     ANITP=NITP-1
     ALPHA1=DEXP(DLOG(1.0/HMIN)/ANITP)
     AOPT(1)=HMIN
     DO 380 IP=2,NITP
     AOPT(IP)=AOPT(IP-1)*ALPHA1
C
     WRITE(2,450)
     WRITE(2,460) AOPT
C
     ********************************
     ---READ INITIAL CONCENTRATIONS AND COMPUTE INITIAL MASS STORED---
     ---IF USING SMALLER SUBGRID FOR TRANSPORT, READ INITIAL
     CONCENTRATION ARRAY FOR SUBGRID NODES ONLY---
     ---READ INITIAL OXYGEN CONCENTRATIONS AND COMPUTE INITIAL
C OXYGEN MASS STORED
READ (1,*) INPUT,FCTR
CFCTR2=2*K*RHOB
DO 420 IY=1,NMY
   JY=IY+MY-1
   IF (INPUT.EQ.1) READ (1,*) (CONC(IY,IX),IX=1,NMX)
   DO 410 IX=1,NMX
      JX=IX+MX-1
      IF (INPUT.EQ.1) GO TO 390
      CONC(IY,IX)=CONC(IY,IX)*FCTR
   GO TO 400
390 IF (THCK(JX,JY).NE.0.0) CONC(IY,IX)=FCTR
400 CONINT(IY,IX)=CONC(IY,IX)
   CFCTR=CONINT(IY,IX)*THCK(JX,JY)*AREA
   SORBI=SORBI+CFCTR*CFCTR2
410 STOMI=STOMI+CFCTR*POROS
420 CONTINUE
READ (1,*) INPUT,FCTR
DO 421 IY=1,NMY
   JY=IY+MY-1
   IF (INPUT.EQ.1) READ (1,*) (CONC1(IY,IX),IX=1,NMX)
   DO 411 IX=1,NMX
      JX=IX+MX-1
      IF (INPUT.EQ.1) GO TO 391
      CONC1(IY,IX)=CONC1(IY,IX)*FCTR
   GO TO 401
391 IF (THCK(JX,JY).NE.0.0) CONC1(IY,IX)=FCTR
401 CONINO(IY,IX)=CONC1(IY,IX)
   CFCTR1=CONINO(IY,IX)*THCK(JX,JY)*AREA
411 STOMIO=STOMIC+CFCTR1*POROS
421 CONTINUE
C **********************************************
C ---CHECK DATA SETS FOR INTERNAL CONSISTENCY---
C DO 440 IX=1,NX
C DO 440 IY=1,NY

CJFH
   IF (CONC1(IY,IX).NE.0.0) BIODEG = .TRUE.

CJFH
   IF (THCK(IY,IX).GT.0.0) GO TO 430
   IF (TMRX(IY,IX,1).GT.0.0) WRITE(2,940) IX,IX
   IF (TMRX(IY,IX,2).GT.0.0) WRITE(2,950) IX,IX
   IF (NODEID(IY,IX).GT.0.0) WRITE(2,960) IX,IX
   IF (WT(IY,IX).NE.0.0) WRITE(2,970) IX,IX
   IF (REC(IY,IX).NE.0.0) WRITE(2,980) IX,IX
   IF (REC(IY,IX).NE.0.0) WRITE(2,990) IX,IX
430 IF (PERM(IY,IX).GT.0.0) GO TO 440
   IF (NODEID(IY,IX).GT.0.0) WRITE(2,1000) IX,IX
   IF (WT(IY,IX).NE.0.0) WRITE(2,1010) IX,IX
   IF (REC(IY,IX).NE.0.0) WRITE(2,1020) IX,IX
   IF (REC(IY,IX).NE.0.0) WRITE(2,1030) IX,IX
   IF (THCK(IY,IX).GT.0.0) WRITE(2,1040) IX,IX
440 CONTINUE
C **********************************************
RETURN
C **********************************************
C
C
450 FORMAT (1H1, 20HITERATION PARAMETERS)
460 FORMAT (3H, 'G20.6')
470 FORMAT (1H1, 27HTIME INTERVALS (IN SECONDS))
475 FORMAT (1H0, 5X, 65H*** WARNING *** INITIAL TIME STEP IS LONGER TH
1AN PUMPING PERIOD/25X, 34H***ADJUST EITHER TINIT OR PINT.***)
480 FORMAT (1H1, 15X, 17HSTEADY-STATE FLOW/5X, 57HTIME INTERVAL (IN SEC)
1 FOR SOLUTE-TRANSPORT SIMULATION = , G12.5)
490 FORMAT (3H, 'G12.5')
500 FORMAT (3H, 'G30.1')
510 FORMAT (1H1, 22HGAUSSIAN THICKNESS (FT))
530 FORMAT (1H1, 30HTRANSMISSIVITY MAP (FT*FT/SEC))
540 FORMAT (40G3.0)
550 FORMAT (I1, G10.0)
560 FORMAT (40G4.1)
570 FORMAT (1H1, 23HNODE IDENTIFICATION MAP/) /
580 FORMAT (1H, 'G30.13')
590 FORMAT (1H1, 45HVERTICAL PERMEABILITY/THICKNESS (FT/(FT*SEC)))
600 FORMAT (1H0, 10X, 12HX-Y SPACING;)
610 FORMAT (1H, 'G12.5')
620 FORMAT (1H1, 24HPERMEABILITY MAP (FT/SEC))
630 FORMAT (1H0, 05X, 05X, 44HNO. OF FINITE-DIFFERENCE CELLS IN AQUIFER =
1, I4//10X, 28HAREA OF AQUIFER IN MODEL = , G12.5, 10H SQ. FT.///1
20X, 47HNCRIT (MAX. NO. OF CELLS THAT CAN BE VOID OF/20X, 56HPARTI
3CLES; IF EXCEEDED, PARTICLES ARE REGENERATED) = , I4//)
633 FORMAT (1H0, ///2X, 26HFLOW MODEL (PRIMARY GRID)://)
634 FORMAT (1H0, ///2X, 18HTRANSPORT SUBGRID://)
635 FORMAT (1H0, 05X, 05X, 44HNO. OF FINITE-DIFFERENCE CELLS IN AQUIFER =
1, I4//10X, 28HAREA OF AQUIFER IN MODEL = , G12.5, 10H SQ. FT./)
640 FORMAT (40I1)
660 FORMAT (40G4.0)
661 FORMAT (40G5.0)
670 FORMAT (1H1, 11HWAUSTRAL TABLE)
680 FORMAT (1H, 'G30.5.0')
690 FORMAT (1H0, 10X, 19HAREA OF ONE CELL = , G12.4)
700 FORMAT (2I2)
710 FORMAT (2I2, 3G8.2)
711 FORMAT (2I2, 3G9.2)
720 FORMAT (10A8)
730 FORMAT (1H0, 10A8)
740 FORMAT (4I4, I5, I3, 12I4)
749 FORMAT (1H1, 3I1, 11HBIOPLUME II)
750 FORMAT (1H1, 74HCONTAMINANT TRANSPORT UNDER THE INFLUENCE OF OXYGEN
1 LIMITED BIODEGRADATION)
755 FORMAT (1H )
760 FORMAT (1H0, 21X, 21HINPUT DATA)
770 FORMAT (1H0, 23X, 16HGRID DESCRIPTORS///13X, 30HNX X (NUMBER OF COLUM
1NS) = , I4//13X, 28HNY (NUMBER OF ROWS) = , I6//13X, 29HXDEL (X
2-DISTANCE IN FEET) = , F7.1/13X, 29HYDEL (Y-DISTANCE IN FEET) = , F7
3.1)
775 FORMAT (1H0, 18X, 31HSECONDARY SUBGRID FOR TRANSPORT///16X, 30HNMX (1
NUMBER OF COLUMNS) = , I4//16X, 30HNMY (NUMBER OF ROWS) = , I
24//16X, 38HCROSS-REF. TO PRIMARY GRID IX IX//46X, 8H --- ///18
3X, 28HFIRST NODE (UPPER LEFT) AT: , 214/18X, 28HLAST NODE (LOWER RIGH
4T) AT: , 214)
1 AT NODE IX =, I4, 6H, IY = I4
950 FORMAT (1H, 5X, 61H*** WARNING *** THCK.EQ.0.0 AND TMRX(Y).GT.0.0
1 AT NODE IX =, I4, 6H, IY = I4)
960 FORMAT (1H, 5X, 61H*** WARNING *** THCK.EQ.0.0 AND NODEID.GT.0.0
1 AT NODE IX =, I4, 6H, IY = I4)
970 FORMAT (1H, 5X, 56H*** WARNING *** THCK.EQ.0.0 AND WT.NE.0.0 AT N
1ODE IX =, I4, 6H, IY = I4)
980 FORMAT (1H, 5X, 58H*** WARNING *** THCK.EQ.0.0 AND RECH.NE.0.0 AT
1 NODE IX =, I4, 6H, IY = I4)
990 FORMAT (1H, 5X, 58H*** WARNING *** THCK.EQ.0.0 AND REC.NE.0.0 AT
1 NODE IX =, I4, 6H, IY = I4)
1000 FORMAT (1H, 5X, 61H*** WARNING *** PERM.EQ.0.0 AND NODEID.GT.0.0
1 AT NODE IX =, I4, 6H, IY = I4)
1010 FORMAT (1H, 5X, 56H*** WARNING *** PERM.EQ.0.0 AND WT.NE.0.0 AT N
1ODE IX =, I4, 6H, IY = I4)
1020 FORMAT (1H, 5X, 58H*** WARNING *** PERM.EQ.0.0 AND RECH.NE.0.0 AT
1 NODE IX =, I4, 6H, IY = I4)
1030 FORMAT (1H, 5X, 58H*** WARNING *** PERM.EQ.0.0 AND REC.NE.0.0 AT
1 NODE IX =, I4, 6H, IY = I4)
1040 FORMAT (1H, 5X, 58H*** WARNING *** PERM.EQ.0.0 AND THCK.GT.0.0 AT
1 NODE IX =, I4, 6H, IY = I4)
1050 FORMAT (1H0, 5X, 45H*** WARNING *** ANFCTR WAS SPECIFIED AS 0.0/23
1X, 34HDEFAULT ACTION: RESET ANFCTR = 1.0)
1060 FORMAT (1I1)
1070 FORMAT (1I0, 4, 3G5.0)
1080 FORMAT (1H1, 5X, 25HSTART PUMPING PERIOD NO., I2//2X, 75HTHE FOLLOWIN
1G TIME STEP, FUMPAGE, AND PRINT PARAMETERS HAVE BEEN REDEFINED://)
1090 FORMAT (1H0, 14X, 9HNTM =, I4/15X, 9HNPNT =, I4/15X, 9HNITP =,
2NPNTVL =, I4/15X, 9HNPDLC =, I4/15X, 9HNPCNV =
40.3/)
1100 FORMAT (1H, 58X, E10.3)
1110 FORMAT (1H1, 5X, 25HSTART PUMPING PERIOD NO., I2//2X, 23HNO PARAMETER
1S REDEFINED://)
CGCR
1230 FORMAT (/1H, 11X, '*** THE FOLLOWING ASSIGNMENTS HAVE BEEN MADE:
1, FOR A RESIDUAL SOURCE:/')
1240 FORMAT (1H, 11X, 'RSCMFSp EOM, MLT, DLTC')
1250 FORMAT (1H, 11X, I5, 9X, F8.4, 4X, F10.4, 4X, F8.4)
1260 FORMAT (/1H, 11X, 'CWL, THETA0, THETAW, ASG, ASD')
1220 FORMAT (1H, 10X, 2F8.4, 2F10.4, F12.2, F10.6/)
CGCR
END
VELO

SUBROUTINE Velo

include params

CJFH

DOUBLE PRECISION DMIN1, DEXP, DLOG, DABS
REAL * TMRX, VRM, HI, HR, HC, HK, WT, REC, RECH, TIM, AOFT, TITLE
REAL * DXINV, DYINV, ARIN, PORN
REAL * XDEL, YDEL, S, AREA, SUMT, RHO, PARAM, TEST, TOL, PINT, HMIN, PYR
REAL * SNEAT, SLK, DI

CJFH

REAL * 8RSIMV, RSC1, RSC2, TRS, TRSC, DRS1, DRS2
REAL * 8TAU, TAUPL, TAU, POR, TAUQ, TAUN, DCMAS, DCMASS, DCMASN, DLMAS
REAL * 8AMASS, BMAS, BMAS2, BMAS1, CONST
REAL * 8CC, CWI, THETAO, THETAW, ASG, ASD, EOM, MLT, RSMAS, DLTC
REAL * 8RCWI, RCWL, RTHO, RTHW, G, D

CJFH

INTEGER RSCMPS

CGCR

COMMON /PRM/ NTIM,NEMP, NPNT, NITP, N, NX, NY, NP, NREC, INT, NNX, NNY, NUMO
1BS, NOV, IMV, NPMAX, ITMAX, NZCRIT, IPRT, NPNT, NPNTN, NPNTV, NPNTN, N
2NPNAV, NPDLN, ICHK
COMMON /PRMC/ NODEID(ZX, Zy), NPCELL(ZX, Zy), NPOLD(ZX, Zy), LIMBO(500),
1XOBS(5), YOBS(5)
COMMON /HEDA/ THCK(ZX, Zy), PERM(ZX, Zy), TMHL(5, 50), TMHS(50), AWFCTR
COMMON /HEDB/ TMRX(ZX, Zy, 2), VRM(ZX, Zy), HI(ZX, Zy), HR(ZX, Zy), HC(ZX,
1Zy), HK(ZX, Zy), WT(ZX, Zy), REC(ZX, Zy), RECH(ZX, Zy), TIM(100), AOFT(20),
2TITLE(10), XDEL, YDEL, S, AREA, SUMT, RHO, PARAM, TOL, PINT, HMIN, PYR
COMMON /HEDC/ MX, MY, MXI, NMY, NZ, NNY, MCXK
COMMON /XINV/ DXINV, DYINV, ARINV, PORN
COMMON /CHMA/ PART(3, 3), CONC(ZX, Zy), TMCN(5, 50), VX(ZX, Zy), VY(ZX
2Zy), CONCT(ZX, Zy), CNRECH(ZX, Zy), POROS, SWTCH, Beta, TIMV, STOR
2ML, CMSM, CMSO, FMN, FIMT, SUMEO, CELDI, DLTR, CSTM
COMMON /CHMC/ SUMC(ZX, Zy), VXBDY(ZX, Zy), VYBDY(ZX, Zy)
COMMON /DFUS/ DISP(ZX, Zy, 4)
COMMON /CHMR/ RF, DK, RN, THAL, DECAY, ADSORB, SORBI, DMSL, CSTM

CGCR

COMMON /RSRC/ CWI(NCP), CWI(NCP), THETAO(NCP), THETAW(NCP), ASG(NCP)
1, ASD(NCP), EOM(ZX, Zy), TAU(ZX, Zy), MLT(ZX, Zy), RSCMPS, RSMAS, DLTC

CGCR

C

*******************************************************
C

CJFH

SAVE

CJFH

---- COMPUTE VELOCITIES AND STORE ----

VMAX=1.0E-10
VMAY=1.0E-10
VMXBD=1.0E-10
VMYBD=1.0E-10
TMV=TIM(N)*1.0E5
LIM=0
MAXX=0
MAXY=0

C
DO 20 IX=1,NX  
DO 20 IY=1,NY  
IF (IX.GT.NMX.OR.IY.GT.NMY) GO TO 12  
DO 10 IZ=1,4  
10 DISP(IX,IY,IZ)=0.0  
C  
12 JCK=0  
IF (IX.LT.(MX-1).OR.IY.LT.(MY-1).OR.IX.GT.(MXX+1).OR.IY.GT.(MYY+1))  
1) JCK=1  
IF (THCK(IX,IY).EQ.0.0) GO TO 20  
RATE=REC(IX,IY)/AREA  
SLEAK=(HK(IX,IY)-WT(IX,IY))*VPRM(IX,IY)  
DIV=RATE+SLEAK+RECH(IX,IY)  
C  
---VELOCITIES AT NODES---  
---X-DIRECTION---  
DHX=HK(IX,1,IY)-HK(IX+1,IY)  
IF (THCK(IX+1,IY).EQ.0.0) DHX=HK(IX,IY)-HK(IX+1,IY)  
IF (THCK(IX-IY).EQ.0.0) DHX=HK(IX-1,IY)-HK(IX,IY)  
IF (THCK(IX,IY).EQ.0.0.AND.THCK(IX+1,IY).EQ.0.0) DHX=0.0  
GRDX=DHX*DXINV*0.50  
VX(IX,IY)=PERM(IX,IY)*GRDX*PORINV  
ABVX=ABS(VX(IX,IY))  
IF (ABVX.GT.VMAX.AND.JCK.EQ.0) VMAX=ABVX  
---Y-DIRECTION---  
DHY=HK(IX,1,IY)-HK(IX,1,IY)  
IF (THCK(IX+1,1,IY).EQ.0.0) DHY=(HK(IX,1,IY)-HK(IX,1,IY+1))  
IF (THCK(IX-IY+1).EQ.0.0) DHY=(HK(IX,1,IY)-HK(IX,1,IY))  
IF (THCK(IX,1,IY).EQ.0.0.AND.THCK(IX,1,IY+1).EQ.0.0) DHY=0.0  
GRDY=DHY*DYINV*0.50  
VY(IX,1,IY)=PERM(IX,1,IY)*GRDY*PORINV*ANFCTR  
ABVY=ABS(VY(IX,1,IY))  
IF (ABVY.GT.VMAY.AND.JCK.EQ.0) VMAY=ABVY  
C  
---VELOCITIES AT CELL BOUNDARIES---  
GRDX=(HK(IX,1,IY)-HK(IX+1,1,IY))*DXINV  
PERMX=2.0*PERM(IX,IY)*PERM(IX+1,IY)/(PERM(IX,IY)+PERM(IX+1,IY))  
VXBDY(IX,IY)=PERMX*GRDX*PORINV  
GRDY=(HK(IX,1,IY)-HK(IX,1,IY+1))*DYINV  
PERMY=2.0*PERM(IX,1,IY)*PERM(IX,1,IY+1)/(PERM(IX,1,IY)+PERM(IX,1,IY+1))  
VYBDY(IX,IY)=PERMY*GRDY*PORINV*ANFCTR  
ABVX=ABS(VXBDY(IX,IY))  
ABVY=ABS(VYBDY(IX,IY))  
IF (ABVX.GT.VMXXB.AND.JCK.EQ.0) VMXXB=ABVX  
IF (ABVY.GT.VMXXB.AND.JCK.EQ.0) VMXXB=ABVY  
C  
IF (DIV.GE.0.0) GO TO 20  
IF (JCK.GT.0) GO TO 20  
TDIV=(POROS*THCK(IX,IY)*RF)/DABS(DIV)  
TDIV1=(POROS*THCK(IX,IY))/DABS(DIV)  
IF (TDIV1.LT.TDIV) TDIV=TDIV1  
IF (TDIV.GE.TMV) GO TO 20  
TMV=TDIV  
MAXX=IX  
MAXX=IY  
20 CONTINUE
C ***************************************************************
C ---PRINT VELOCITIES---
IF (NPNTVL.EQ.0) GO TO 80
IF (NPNTVL.EQ.2) GO TO 30
IF (NPNTVL.EQ.1.AND.N.EQ.1) GO TO 30
GO TO 80
30 WRITE(2,320)
   WRITE(2,330)
   DO 40 IY=1,NY
40 WRITE(2,350) (VX(IX,IY),IX=1,NX)
   WRITE(2,340)
   DO 50 IY=1,NY
50 WRITE(2,350) (VXBDY(IX,IY),IX=1,NX)
   WRITE(2,360)
   WRITE(2,330)
   DO 60 IY=1,NY
60 WRITE(2,350) (VY(IX,IY),IX=1,NX)
   WRITE(2,340)
   DO 70 IY=1,NY
70 WRITE(2,350) (VYBDY(IX,IY),IX=1,NX)
C ---PUNCH VELOCITIES---
80 IF (NPNCHE.EQ.0) GO TO 110
   IF (NPNCHE.EQ.2) GO TO 90
   IF (NPNCHE.EQ.1.AND.N.EQ.1) GO TO 90
   GO TO 110
90 WRITE (7,510) NX,NY,XDEL,YDEL,VMAX,VMAY
   DO 100 IY=1,NY
100 WRITE (7,520) (VX(IX,IY),IX=1,NX)
   WRITE (7,520) (VY(IX,IY),IX=1,NX)
C ---COMPUTE NEXT TIME STEP---
110 WRITE(2,390)
   WRITE(2,392)
   WRITE(2,400) VMAX,VMAY
   WRITE(2,410) VMXBD,VMYBD
   IF (RF.LE.1.0) GO TO 115
115 WRITE(2,394)
   VMAX1=VMAX
   VMAY1=VMAY
   VMXBD1=VMXBD
   VMYBD1=VMYBD
   TDELX1=CELDIS*XDEL/VMAX1
   TDELY1=CELDIS*YDEL/VMAY1
   TDLX1=CELDIS*XDEL/VMXBD1
   TDLY1=CELDIS*YDEL/VMYBD1
   TIMV=AMIN1(TDELX1,TDELY1,TDLX1,TDLY1)
   VMAX=VMAX/RF
   VMAY=VMAY/RF
   VMXBD=VMXBD/RF
   VMYBD=VMYBD/RF
   WRITE(2,400) VMAX,VMAY
   WRITE(2,410) VMXBD,VMYBD
   WRITE(2,396)
115 WRITE(2,400) VMAX1,VMAY1
   WRITE(2,410) VMXBD1,VMYBD1
   IF (AMAX1(VMAX,VMAY,VMXBD,VMYBD).LE.1.0E-10) WRITE(2,570)
IF (AMAX1(VMAX1,VMAX1,VMXBD1,VMYBD1).LE.1.0E-10) WRITE(2,570)
GO TO 116
115 TDELX=CELDIS*XDEL/VMAX
TDELY=CELDIS*YDEL/VMAX
TDELXB=CELDIS*XDEL/VMXBD
TDELYB=CELDIS*YDEL/VMYBD
TIMV=AMIN1(TDELX,TDELY,TDELXB,TDELYB)
IF (AMAX1(VMAX,VMAX,VMXBD,VMYBD).LE.1.0E-10) WRITE(2,570)
116 WRITE(2,310) TIMV,TIMV
IF (TIMV.LT.TIMV) GO TO 120
LIM=-1
GO TO 130
120 TIMV=TIMV
LIM=1
130 NTIMV=TIM(N)/TIMV
NMOV=NTIMV+1
WRITE(2,420) TIMV,NTIMV,NMOV
TIMV=TIM(N)/NMOV
WRITE(2,370) TIM(N)
WRITE(2,380) TIMV
C
IF (BETA.EQ.0.0) GO TO 200
C
***********COMPUTE DISPERSION COEFFICIENTS***********
C
ALPHA=BETA
ALNG=ALPHA
TRAN=DLTRAT*ALPHA
XX2=XDEL*XDEL
YY2=YDEL*YDEL
XY2=4.0*XDEL*YDEL
DO 150 IX=2,MAX
DO 150 IY=2,MMY
IF (THCK(IX,IY).EQ.0.0) GO TO 150
JX=IX-MX+1
JY=IY-MY+1
IF (JX.LT.1.OR.JY.LT.1) GO TO 150
VXE=VXBDY(IX,IY)
VYS=VYBDY(IX,IY)
IF (THCK(IX+1,IY).EQ.0.0) GO TO 140
IF ((IX+1).GT.MXX) GO TO 140
C
---FORWARD COEFFICIENTS: X-DIRECTION---
VYE=(VYBDY(IX,IY-1)+VYBDY(IX+1,IY-1)+VYS+VYBDY(IX+1,IY))/4.0
VXE2=VXE*VXE
VYE2=VYE*VYE
VMGE=SQRT(VXE2+VYE2)
IF (VMGE.LT.1.0E-20) GO TO 140
DALN=ALNG*VMGE
DTRN=TRAN*VMGE
VMGE2=VMGE*VMGE
C
---XX COEFFICIENT---
DISP(JX,JY,1)=(DALN*VXE2+DTRN*VYE2)/(VMGE2*XX2)
C
---XY COEFFICIENT---
IF ((IY-1).LT.MY.OR.(IY+1).GT.MMY) GO TO 140
DISP(JX,JY,3)=(DALN-DTRN)*VXE*VYE/(VMGE2*XY2)
C
---FORWARD COEFFICIENTS: Y-DIRECTION---
140 IF (THCK(IX,IY+1).EQ.0.0) GO TO 150
IF ((IY+1).GT.MMY) GO TO 150
VXS=(VXBDY(I-1,IY)+VXEB+VXBDY(I-1,IY+1)+VXBDY(I,IY+1))/4.0
VYS=VXS*VYS
VXS2=VXS*VXS
VMGS=SQRT(VXS2+VYS2)
IF (VMGS.LT.1.0E-20) GO TO 150
DALN=ALNG*VMGS
DTRN=TRAN*VMGS
VMGS2=VMGS*VMGS
C
---YY COEFFICIENT---
DISP(JX,JY,2)=(DALN*VYS2+DTRN*VXS2)/(VMGS2*YY2)
C
---XY COEFFICIENT---
IF ((IX-1).LT.MX.OR.(IX+1).GT.MMX) GO TO 150
DISP(JX,JY,4)=(DALN-DTRN)*VXS*VYS/(VMGS2*XY2)
150 CONTINUE
C
********************************************************************
C
---ADJUST CROSS-PRODUCT TERMS FOR ZERO THICKNESS---
DO 160 IX=2,MMX
DO 160 IY=2,MMY
JX=IX-MX+1
JY=IY-MY+1
IF (JX.LT.1.OR.JY.LT.1) GO TO 160
IF (THCK(IX,IX,1),EQ.0.0) THCK(IX,IX,1),EQ.0.0 THCK(IX,IX,1)
160 CONTINUE
C
********************************************************************
C
---CHECK FOR STABILITY OF EXPLICIT METHOD---
TIMDIS=0.0
DO 170 IX=1,MMX
DO 170 IY=1,MMY
TDCO=(DISP(IX,IX,1)+DISP(IX,IX,2))/RF
TDCO1=(DISP(IX,IX,1)+DISP(IX,IX,2))
IF (TDCO.LT.TDCO1) TDCO=TDCO1
170 IF (TDCO.GT.TIMDIS) TIMDIS=TDCO
TIMDC=0.5/TIMDIS
WRITE(2,440) TIMDC
NTIMD=TIM(N)/TIMDC
NDISP=NTIMD+1
IF (NDISP.LE.NMOV) GO TO 180
NMOV=NDISP
TIMV=TIM(N)/NMOV
LIM=0
180 WRITE(2,430) TIMV,NTIMD,NMOV
C
********************************************************************
C
---ADJUST DISP. EQUATION COEFFICIENTS FOR SATURATED THICKNESS---
DO 190 IX=2,MMX
DO 190 IY=2,MMY
IF (THCK(IX,IX),EQ.0.0) GO TO 190
JX=IX-MX+1
JY=IY-MY+1
IF (JX.LT.1.OR.JY.LT.1) GO TO 190
BAXX=2.0*THCK(IX,IX)*THCK(IX+1,IX)/(THCK(IX,IX)+THCK(IX+1,IX))
BAYY=2.0*THCK(IX,IX)*THCK(IX,IX+1)/(THCK(IX,IX)+THCK(IX,IX+1))
DISP(JX,JY,1)=DISP(JX,JY,1)*BAXX
DISP(JX, JY, 2) = DISP(JX, JY, 2) * BAVY
DISP(JX, JY, 3) = DISP(JX, JY, 3) * BAVX
DISP(JX, JY, 4) = DISP(JX, JY, 4) * BAVY
CONTINUE
C

CGR
--- DETERMINE MAXIMUM TIME STEP DUE TO A RESIDUAL SOURCE ---
IF (RSCMPS .LT. 1) GO TO 200
MI = 1
DO 192 IX = 1, NX
DO 192 IY = 1, NY
IF (EOM(IX, IY) .EQ. 0.0) GO TO 192
RECH(IX, IY) = RECH(IX, IY) * MLT(IX, IY)
WRITE (2, 610) IX, IY
C
DO 194 NI = MI, ITMAX
RSTIMV = TIM(N) / NI
TAUO = TAU(IX, IY)
WRITE (2, 620) TIM(N), NI, RSTIMV
C
DO 196 KI = 1, NI
RSC1 = 0.0
RSC2 = 0.0
DLMASS = 0.0
WRITE (2, 630) KI, TAUO
C
DO 198 IJ = 1, RSCMPS
RCWI = CWI(IJ)
RCWL = CWL(IJ)
RTHO = THETAO(IJ)
RTHW = THETAW(IJ)
G = ASG(IJ)
D = ASD(IJ)
TAUPL = 1.0 + (RTHO / RTHW) * G * D * RCWI ** (D - 1.0)
TAUL = 1.0 + (RTHO / RTHW) * G * D * RCWL ** (D - 1.0)
PORV = EOM(IX, IY) * RTHW * AREA
AMASS = RCWI * TAUPL * PORV
CONST = (RTHW / RTHO) ** (1.0 / (D - 1.0)) * PORV
BMASSE1 = CONST * (D - 1.0) / D * (TAUPL - 1.0) ** (D / (D - 1.0))
BMASSE2 = CONST * (D - 1.0) / D * (TAUL - 1.0) ** (D / (D - 1.0))
BMASS = BMASSE2 - BMASSE1
C
IF (TAUO .LE. TAUPL) THEN
DCMASS = TAUO * RCWI * PORV
ELSE
IF (TAUO .GE. TAUL) THEN
DCMASS = AMASS + BMASSE + (TAUO - TAUL) * RCWL * PORV
ELSE
DCMASS = AMASS + (CONST * (D - 1.0) / D * (TAUO - 1.0) ** (D / (D - 1.0)) - BMASSE1)
ENDIF
ENDIF
C
TAUN = TAUO + RSTIMV * (-RECH(IX, IY) * AREA / PORV)
IF (TAUN .LE. TAUPL) THEN
DCMASSN = TAUN * RCWI * PORV
ELSE
ENDIF
IF (TAUN. GE. TAUPL) THEN
DCMSSN = AMASS + BMASS + (TAUN-TAUL)*RCWL*FORV
ELSE
DCMSSN = AMASS + (CONST*(D-1.0)/D*
(TAUN-1.0)**(D/(D-1.0)) - BMASS1)
ENDIF
ENDIF
DLMSS = DLMSS + (DCMSSN - DCMSS)
C
IF (TAU0.LE.TAUPL) THEN
RSC1 = RSC1 + RCWI
ELSE
IF (TAU0.GE.TAUL) THEN
RSC1 = RSC1 + RCW1
ELSE
RSC1 = RSC1 + ((TAU0-1.0)*RTHW/(RTHO*G*D))**(1.0/(D-1.0))
ENDIF
ENDIF
IF (TAU0.LE.TAUPL) THEN
RSC2 = RSC2 + RCWI
ELSE
IF (TAU0.GE.TAUL) THEN
RSC2 = RSC2 + RCW1
ELSE
RSC2 = RSC2 + ((TAU0-1.0)*RTHW/(RTHO*G*D))**(1.0/(D-1.0))
ENDIF
ENDIF
198 CONTINUE
TSRSC = DLMSS / (-RECH(IX,IY)*AREA*RSTIMV)
DRSC1 = (RSC1-TSRSC)/RSC1
DRSC2 = (TSRSC-RSC2)/TSRSC
WRITE(2,640)RSC1,TSRSC,RSC2
WRITE(2,650)DRSC1,DRSC2,DLTC
IF (DRSC1.GT.DLTC .OR. DRSC2.GT.DLTC) GO TO 194
TAU0 = TAUN
196 CONTINUE
MI = NI
WRITE(2,660)MI
RECH(IX,IY) = RECH(IX,IY)/MLT(IX,IY)
GO TO 192
194 CONTINUE
MI = NI-1
WRITE(2,670)MI
RECH(IX,IY) = RECH(IX,IY)/MLT(IX,IY)
192 CONTINUE
C
WRITE(2,710)RSTIMV
IF (TIMV.LT.RSTIMV) GO TO 200
TIMV = RSTIMV
NTIMV = MI
NMOV = MI
WRITE(2,420)TIMV,NTIMV,NMOV
IF (NMOV.EQ.1) GO TO 235
WRITE(2,720)
GO TO 240
CGCR ****************************
C
200 IF (NMOV.EQ.1) GO TO 235
   IF (LIM) 210,220,230
210 WRITE(2,530)
   GO TO 240
220 WRITE(2,540)
   GO TO 240
230 WRITE(2,550)
   WRITE(2,560) MAXX,MAXY
   GO TO 240
235 WRITE(2,580)
C
******************************************************************************
C
---PRINT DISPERSION EQUATION COEFFICIENTS---
240 IF (NPNTD.EQ.0) GO TO 300
   IF (NPNTD.EQ.2) GO TO 250
   IF (NPNTD.EQ.1.AND.N.EQ.1) GO TO 250
   GO TO 300
250 WRITE(2,450)
   WRITE(2,460)
   DO 260 IY=1,NMY
260 WRITE(2,500) (DISP(IX,IY,1),IX=1,NMX)
   WRITE(2,470)
   DO 270 IY=1,NMY
270 WRITE(2,500) (DISP(IX,IY,2),IX=1,NMX)
   WRITE(2,480)
   DO 280 IY=1,NMY
280 WRITE(2,500) (DISP(IX,IY,3),IX=1,NMX)
   WRITE(2,490)
   DO 290 IY=1,NMY
290 WRITE(2,500) (DISP(IX,IY,4),IX=1,NMX)
C
******************************************************************************
C
C
C
310 FORMAT (1H0,19H TMV (MAX. INJ.) = ,G12.5/20H TIMV (CELDIS) = ,G
       112.5)
320 FORMAT (1H1,12HX VELOCITIES)
330 FORMAT (1H ,25X,8HAT NODES/)
340 FORMAT (1H0,25X,13HON BOUNDARIES/)
350 FORMAT (1H ,1P10E12.3)
360 FORMAT (1H1,12HY VELOCITIES)
370 FORMAT (3H ,11HTIM (N) = ,1G12.5)
380 FORMAT (3H ,11HTIMEVELO = ,1G12.5)
390 FORMAT (1H1,10X,29HSTABILITY CRITERIA --- M.O.C./)
392 FORMAT (1H0,5X,16HFLUID VELOCITIES)
394 FORMAT (1H0,5X,27HEFFECTIVE SOLUTE VELOCITIES)
396 FORMAT (1H0,5X,27HEFFECTIVE OXYGEN VELOCITIES)
400 FORMAT (1H ,8H VMAX = ,1PE9.2,5X,7HVMAY = ,1PE9.2)
410 FORMAT (1H ,8H VMXB= ,1PE9.2,5X,7HVMYBD= ,1PE9.2)
420 FORMAT (1H1,8H TIMV = ,1PE9.2,5X,8HNTIMV = ,I5,5X,7HNMAY = ,I5/)
430 FORMAT (1H1,8H TIMV = ,1PE9.2,5X,8HNTIMD = ,I5,5X,7HNMAY = ,I5)
440 FORMAT (3H ,11HTIMEDISP = ,1E12.5)
450 FORMAT (1H1,32H DISPERSION EQUATION COEFFICIENTS,10X,25H=(D-IJ)*(B)
1/(GRID FACTOR))
460 FORMAT (1H,35X,14HXX COEFFICIENT/)
470 FORMAT (1H,35X,14HYY COEFFICIENT/)
480 FORMAT (1H,35X,14HXY COEFFICIENT/)
490 FORMAT (1H,35X,14HYX COEFFICIENT/)
500 FORMAT (1H,1P10E11.2)
510 FORMAT (2I4,2F10.1,2F10.7)
520 FORMAT (6F10.7)
530 FORMAT (1H,10X,42H THE LIMITING STABILITY CRITERION IS CELDIS)
540 FORMAT (1H,10X,40H THE LIMITING STABILITY CRITERION IS BETA)
550 FORMAT (1H,10X,58H THE LIMITING STABILITY CRITERION IS MAXIMUM INJECTION RATE)
560 FORMAT (1H,15X,35HMAX. INJECTION OCCURS AT CELL IX = ,I3,7H IY = 1,I3)
570 FORMAT (1H,5X,47H*** WARNING *** DECREASE CRITERIA IN E 230-260)
580 FORMAT (1H,10X,63H*TIME INCREMENT FOR SOLUTE TRANSPORT EQUALS TIM 1E STEP FOR FLOW*)

CGCR
610 FORMAT (/3H ,3X,'CHECK CELL (',I2,','I2,')')
620 FORMAT (3H ,6X,'TIM(N) = ',G10.4,5X,'NI = ',I5,5X
1,'RSTIMV = ',G10.4)
630 FORMAT (3H ,9X,'INTERVAL = ',I5,5X,'TAUO = ',G10.4)
640 FORMAT (3H ,12X,'RSC1 = ',G10.4,5X,'TSRSC = ',G10.4,5X
1,'RSC2 = ',G10.4)
650 FORMAT (3H ,12X,'DRSC1 = ',G10.4,5X,'DRSC2 = ',G10.4,5X
1,'DITC = ',G10.4)
660 FORMAT (3H ,9X,'MI = ',I5,5X,'ALL INTERVALS CHECK OUT OK 1, GO TO NEXT CELL')
670 FORMAT (3H ,6X,'MI = ',I5,5X,'ITMAX REACHED')
710 FORMAT (3H ,11H TIMERESS = ,1G12.5)
720 FORMAT (1H,10X,84H THE LIMITING STABILITY CRITERION IS CHANGE IN RESIDUAL SOURCE LEACHATE CONCENTRATION)

CGCR
END
MOVE

SUBROUTINE MOVE

include params

REAL *8TRX, VRPM, HI, HR, HC, WK, WT, REC, RECH, TIM, AOPT, TITLE
REAL *8XDEL, YDEL, S, AREA, SUMT, RHO, PARAM, TEST, TOL, PINT, HMIN, PYR

REAL *8CWI, CWL, THETA0, THETAW, ASG, ASD, EOM, TAU, MLT, RSMASS, DLTC

LOGICAL BIOUS

COMMON /PRMJ/ NTIM, NPMP, NPTNT, NTIT, N, NX, NY, NP, NREC, INT, NNX, NNY, NUMO
1BS, NM0V, IMOV, NMAX, ITMAX, NZCRI1, IPRNT, NPTPND, NPNTMV, NPNTV1, NPNTD, N
2PNCHV, NPDEL, ICHK

COMMON /PRMJ1/ NP1, IPRNT1

COMMON /PRMC/ NODEID (ZX, ZY), NPCELL (ZX, ZY), NPOLD (ZX, ZY), LIMBO (500),
1IXOBS (5), IYOBS (5)

COMMON /HEDA/ THCK (ZX, ZY), PERM (ZX, ZY), TMWL (5, 50), TMOB (50), ANFCTR

COMMON /HEDB/ TMIX (ZX, ZY, 2), VRPM (ZX, ZY), HI (ZX, ZY), HR (ZX, ZY), HC (ZX,
1ZY), HN (ZX, ZY), WT (ZX, ZY), REC (ZX, ZY), RCCH (ZX, ZY), TIM (100), AOPT (20),
2TITLE (10), XDEL, YDEL, S, AREA, SUMT, RHO, PARAM, TEST, TOL, PINT, HMIN, PYR

COMMON /HEDC/ MX, MY, MMX, MMY, NMX, NMY, MCHK

COMMON /CHMA/ PART (3, ZP), CONC (ZX, ZY), TMCN (5, 50), VX (ZX, ZY), VY (ZX,
1, ZY), CONINT (ZX, ZY), CNRECH (ZX, ZY), PENOS, SUMTH, BETM, TMV, STORM, STOR
2MI, CMSIN, CMSOUT, FIMIN, FLMOT, SUMIO, CELDIL, DLTRAT, CSTORM

COMMON /CHMA1/ PART (3, ZP), CONC1 (ZX, ZY), TMCN1 (5, 50), CONINO (ZX, ZY,
1), CNRECO (ZX, ZY), STORM1, STOMIO, CMSIN1, CMSOUT1, FIMIN1, FLMOT1, SUMIO1, 
2STORO

COMMON /JFH/ BIOUS

COMMON /RSSC/ CWI (NCP), CWL (NCP), THETA0 (NCP), THETAW (NCP), ASG (NCP)
1, ASD (NCP), EOM (ZX, ZY), TAU (ZX, ZY), MLT (ZX, ZY), RSCMPS, RSMASS, DLTC

****************************************************************************************

INTEGER*4 toolbx
INTEGER*4 ERASERECT
INTEGER*4 MOVETO
PARAMETER (ERASERECT = 'Z'8A330000')
PARAMETER (MOVETO = 'Z'89309000')
INTEGER*2 rect (4)

INTEGER RSCMPS

SAVE

WRITE (2, 680) NM0V

Write some info to the screen
CJFH
rect(1) = 120
rect(2) = 0
rect(3) = 500
rect(4) = 600
call toolbox(MOVETO,10,120)
IF (BIODEG) THEN
    WRITE(*,*) 'Including oxygen computations'
ELSE
    WRITE(*,*) 'Excluding oxygen computations'
END IF
call toolbox(MOVETO,10,135)
WRITE(*,*) 'Time step number ... ',N
call toolbox(MOVETO,10,150)
WRITE(*,*) 'Number of particle moves required ... ',NMOV
WRITE(*,*)

CJFH
SUMTCH=SUMT-TIM(N)
C ---MOVE PARTICLES 'NMOV' TIMES---
DO 650 IMOV=1,NMOV

CJFH
rect(1) = 160
rect(2) = 0
rect(3) = 600
rect(4) = 600
call toolbox(ERASERECT,rect)
call toolbox(MOVETO,10,160)
WRITE(*,*) 'Computing move number ... ',IMOV

CGCR
IF (RSCMPS.GT.0) CALL ASMOD

CGCR
CALL MOVEH
IF (BIODEG) THEN
    CALL MOVEO
END IF
CALL ADDPLM

C **********************************************************
C ---STORE OBS. WELL DATA FOR STEADY FLOW PROBLEMS---
IF (S.GT.0.0) GO TO 640
IF (NUMOBS.LE.0) GO TO 640
J=MOD(IMOV,50)
IF (J.EQ.0) J=50
TMOBS(J)=SUMTCH
DO 630 I=1,NUMOBS
TMWL(I,J)=HK(I,IXOBS(I),IYOBS(I))
IX=IXOBS(I)-MX+1
IF (IXOBS(I).LT.MX.OR.IXOBS(I).GT.MMX) GO TO 630
TY=IYOBS(I)-MY+1
IF (IYOBS(I).LT.MY.OR.IYOBS(I).GT.MMY) GO TO 630
TMCN(I,J)=CONC(IX,IX)
TMCM(I,J)=CONCM(IX,IX)
630 CONTINUE

C ---PRINT CHEMICAL OUTPUT---
IF (MOD(IMOV,50).EQ.0) IFRNT=1
IF (MOD(IMOV,50).EQ.0) IFRNT1=1
640 IF (IMOV.GE.NMOV) GO TO 660
   IF (MOD(IMOV,NPTMNV).EQ.0) IPRNT=-1
   IF (MOD(IMOV,NPTMNV).EQ.0) IPRNT1=-1
C
C   **************************************************************************
C   IF (IPRNT.NE.0) CALL CHMOT
CJFH   IF (((IPRNT1.NE.0).AND.(BIODEG)) CALL CHMOT1
CJFH
C   650 CONTINUE
C   660 RETURN
C   680 FORMAT (1H0,10X,61HNO. OF PARTICLE MOVES REQUIRED TO COMPLETE THIS
          1 TIME STEP = ,I4//)
C   END
SUBROUTINE CHMOT

include params

REAL *8 TMRX, VRPM, HI, HR, HC, HK, WT, RECH, TIM, AOPT, TITLE
REAL *8 XDEL, YDEL, S, AREA, SUMT, RHO, PARAM, TEST, TOL, PINT, HMIN, PYR

REAL *8 CWI, CWL, THETAO, THETAW, ASG, ASD, EOM, TAU, MLT, RSMASS, DLTC
INTEGER RSCMPS

COMMON /PRMJ/ NTIM, NPMP, NPNT, NINTP, N, NX, NY, NP, NREC, INT, NNX, NNY, NUMO
1BS, NMOV, IMOV, NPMAX, ITMAX, N2CRT, IPRNT, NPTN, NPTMV, NPTNL, NPN, N2PCHV, NPDEL, ICHK
COMMON /PRMC/ NODEID (ZX, ZY), NCCELL (ZX, ZY), NNPOLD (ZX, ZY), LIMBO (500),
1IXOBS (5), IYOBS (5)
COMMON /HEDB/ THCK (ZX, ZY), PERM (ZX, ZY), TMWL (5, 50), TMABS (50), ANFCTR
COMMON /HEDB/ TMRX (ZX, ZY, 2), VRPM (ZX, ZY), HI (ZX, ZY), HR (ZX, ZY), HC (ZX,
1ZY), HK (ZX, ZY), WT (ZX, ZY), RECH (ZX, ZY), RECH (ZX, ZY), TIM (100), AOPT (20),
2TITLE (10), XDEL, YDEL, S, AREA, SUMT, RHO, PARAM, TEST, TOL, PINT, HMIN, PYR
COMMON /HEDC/ MX, MY, MXX, MYY, NMX, NMY, NCHK
COMMON /CHMA/ PART (3, ZP), CONC (ZX, ZY), TMCHN (5, 50), VX (ZX, ZY), VY (ZX
1, ZY), CONINT (ZX, ZY), CNRECH (ZX, ZY), POROS, SUMTCH, BETA, TIMV, STORM, STOR
2MI, CMSIN, CMSOUT, FLMIN, FLMOUT, SUMINO, CELDIS, DLTRAT, CSTM
COMMON /CHMR/ RF, DK, RHOH, THALF, DECAY, ADSORB, SORB, DMSS1, DMSS2, DMSS3
COMMON /DCAY/ DEC1, DEC2, DEC3, DMSS2, DMSS3
COMMON /REAC/ REACT, REACTO

COMMON /RSRC/ CWI (NCP), CWL (NCP), THETAO (NCP), THETAW (NCP), ASG (NCP)
1, ASD (NCP), EOM (ZX, ZY), TAU (ZX, ZY), MLT (ZX, ZY), RSMASS, RSMASS, DLTC

DIMENSION IC (2Z)

C  *****************************************************************************************
C
C  SAVE
C
C
TMFY=86400.0*365.25
TMYR=SUMT/TMFY
TCHD=SUMTCH/86400.0
TCHYR=SUMTCH/TMFY
ERR1=0.0
ERR3=0.0
IF (IPRNT.GT.0) GO TO 100

C  *****************************************************************************************
C
C  ---PRINT CONCENTRATIONS---
WRITE (2, 160)
WRITE (2, 170) N
IF (N.GT.0) WRITE (2, 180) TIM(N)
WRITE (2, 190) SUMT
WRITE (2, 450) SUMTCH
WRITE (2, 200) TCHD
WRITE (2, 210) TMYR
WRITE (2, 460) TCHYR
WRITE(2,380) IMOV
WRITE(2,220)
DO 20 IY=1,NMY
DO 10 IX=1,NMX
10 IC(IX)=CONC(IX,IY)+0.5
CJFH
WRITE(3,*)(CONC(IX,IY),IX=1,NMX)
CJFH
20 WRITE(2,240)(IC(IX),IX=1,NMX)
C
******************************************************
CJFH
IF (N.EQ.0) THEN
   WRITE(3,*),0.0
   WRITE(3,*),STORMI
END IF
CJFH
IF (N.EQ.0) GO TO 150
IF (NPDEL.C.EQ.0) GO TO 50
C
---PRINT CHANGES IN CONCENTRATION---
WRITE(2,230)
WRITE(2,170) N
WRITE(2,180) TIM(N)
WRITE(2,190) SUMT
WRITE(2,450) SUMCH
WRITE(2,200) TCHD
WRITE(2,210) TMYR
WRITE(2,460) TCHYR
WRITE(2,380) IMOV
WRITE(2,220)
DO 40 IY=1,NMY
DO 30 IX=1,NMX
CNG=CONC(IX,IY)-CONINT(IX,IY)
30 IC(IX)=CNG
40 WRITE(2,240)(IC(IX),IX=1,NMX)
C
******************************************************
C
---PRINT MASS BALANCE DATA FOR SOLUTE---
50 RESID=SUMIO-CSTM2+DMASS1+DMASS2+DMASS3
SUMIN=FLMIN-CMSIN
IF (SUMIN.EQ.0.0) GO TO 60
ERR1=RESID*100.0/SUMIN
IF (SUMIO.GT.(STORMI+SORBI)) GO TO 70
60 IF (STORMI.EQ.0.0) GO TO 70
ERR3=-100.0*(RESID)/(STORMI+SORBI-SUMIO)
70 WRITE(2,220)
WRITE(2,250)
WRITE(2,220)
WRITE(2,260) FLMIN
WRITE(2,270) FLMOT
RECI=-CMSIN
RECOUT=-CMSOUT
STORM=STORM-REACTH
WRITE(2,290) RECI
CGCR
WRITE(2,292) RSMASS
CGCR
WRITE(2,280) RECCOUT
WRITE(2,281) REACTH
WRITE(2,295) DMASS1
WRITE(2,297) DMASS2
WRITE(2,299) DMASS3
WRITE(2,296) ADSORB
WRITE(2,298) SORBI
WRITE(2,300) SUMIO
WRITE(2,310) STORMI
WRITE(2,320) STORM
WRITE(2,330) CSTORM
WRITE(2,332) CSTM2
WRITE(2,340)
WRITE(2,350) RESID
WRITE(2,360) ERR1
CJFH
IF (ABS(ERR3) .GT. ABS(ERR1)) THEN
   WRITE(3,*) ERR3
ELSE
   WRITE(3,*) ERR1
END IF
WRITE(3,*) STORM
CJFH
80 IF (STORMI.EQ.0.0) GO TO 90
   IF (SUMIN.NE.0.0 .AND. SUMIO.GT.(STORMI+SORBI)) GO TO 90
   WRITE(2,370)
   WRITE(2,360) ERR3
C
*****************************************************************************************
C
---PRINT HYDROGRAPHS AFTER 50 STEPS OR END OF SIMULATION---

90 IF (MOD(IMOV,50).EQ.0 .AND. S.EQ.0.0) GO TO 100
   IF (MOD(N,50).EQ.0 .AND. S.GT.0.0) GO TO 100
   IF (S.EQ.0.0 .AND. N.LT.NTIM .AND. INT.GT.0) GO TO 100
   GO TO 150

100 WRITE(2,390) TITLE
   IF (NUMOBS.LE.0) GO TO 150
   WRITE(2,400) INT
   IF (S.GT.0.0) WRITE(2,410)
   IF (S.EQ.0.0) WRITE(2,420)
C
---TABULATE HYDROGRAPH DATA---
MOZ=0
   IF (S.GT.0.0) GO TO 110
   NT0=NM0V
   IF (NM0V.GT.50) NT0=MOD(IMOV,50)
   GO TO 120
110 NT0=NTIM
   IF (NTIM.GT.50) NT0=MOD(N,50)
120 IF (NT0.EQ.0) NT0=50
   DO 140 J=1,NUMOBS
   T0YR=0.0
   JX=IXOBS(J)
   JY=IYOBS(J)
   WRITE(2,430) J,IXOBS(J),IYOBS(J)
   C1NT=0.0
   IX=JX-MX+1
   IY=JY-MY+1
   IF (JX.LT.MX.OR.JY.LT.MY.OR.JX.GT.MMX.OR.JY.GT.MMY) GO TO 125
   DO 130 K=1,NUMOBS
   IF (IX.EQ.K) GO TO 130
130 IF (JX.LT.MMX.OR.JY.LT.MM) GO TO 130
   WRITE(2,440) J,IXOBS(J),IYOBS(J)
   C1NT=0.0
   IX=JX-MX+1
   IY=JY-MY+1
   IF (JX.LT.MMX.OR.JY.LT.MM) GO TO 130
   IF (JX.EQ.K) GO TO 130
140 CONTINUE
C
---END---
CLINT=CONINT(IX, IY)
GO TO 127
125 WRITE (2, 435)
127 WRITE (2, 440) MOZ, WT(JX, JY), CLINT,
1TMYR
DO 130 M=1, NTO
TMYR=TMY(S)(M)/TMFY
130 WRITE (2, 440) M, TMWL(J, M), TMCN(J, M), TMYR
140 CONTINUE
C
******************************************************************************
150 IPRINT=0
RETURN
******************************************************************************
C
C
160 FORMAT (1H1, 28HCONCENTRATION OF CONTAMINANT/)
170 FORMAT (1X, 23HNUMBER OF TIME STEPS = , I5)
180 FORMAT (8X, 16HDELTA T = , 1G12.5)
190 FORMAT (8X, 16HTIME (SECONDS) = , 1G12.5)
200 FORMAT (3X, 21HCHEM. TIME (DAYS) = , 1E12.5)
210 FORMAT (8X, 16HTIME (YEARS) = , 1E12.5)
220 FORMAT (1H )
230 FORMAT (1H1, 23HCHANGE IN CONCENTRATION/)
240 FORMAT (1H0, 30I5)
250 FORMAT (1H, 21HCHEMICAL MASS BALANCE)
260 FORMAT (8X, 25HMASS IN BOUNDARIES = , 1E12.5)
270 FORMAT (8X, 25HMASS OUT BOUNDARIES = , 1E12.5)
280 FORMAT (8X, 25HMASS PUMPED OUT = , 1E12.5)
281 FORMAT (8X, 25HMASS LOST W. BIODEG. = , 1E12.5)
290 FORMAT (8X, 25HMASS PUMPED IN = , 1E12.5)
C
292 FORMAT (8X, 25H * FROM RESIDUAL SOURCE = , 1E12.5)
C
295 FORMAT (8X, 25HMASS LOST BY RADIO. DCY= , 1E12.5)
296 FORMAT (8X, 25HMASS ADSORBED ON SOLIDS= , 1E12.5)
298 FORMAT (8X, 25HINITIAL MASS ADSORBED = , 1E12.5)
297 FORMAT (8X, 25HMASS LOST BY ANAER. DCY= , 1E12.5)
299 FORMAT (8X, 25HMASS LOST BY REAER. DCY= , 1E12.5)
300 FORMAT (8X, 25HINFLOW MINUS OUTFLOW = , 1E12.5)
310 FORMAT (8X, 25HINITIAL MASS DISSOLVED = , 1E12.5)
320 FORMAT (8X, 25HPRESENT MASS DISSOLVED = , 1E12.5)
330 FORMAT (8X, 25HCHANGE MASS DISSOLVED = , 1E12.5)
332 FORMAT (8X, 25HCHANGE TOTL.MASS STORED= , 1E12.5)
340 FORMAT (1H , 5X, 53HCOMPARE RESIDUAL WITH NET FLUX AND MASS ACCUMULA
1TION;)
350 FORMAT (8X, 25HMASS BALANCE RESIDUAL = , 1E12.5)
360 FORMAT (8X, 25HERROR (AS PERCENT) = , 1E12.5)
370 FORMAT (1H , 5X, 55HCOMPARE INITIAL MASS STORED WITH CHANGE IN MASS
1STORED;)
380 FORMAT (1X, 23H NO. MOVES COMPLETED = , I5)
390 FORMAT (1H11, 10A8//)
400 FORMAT (1H0, 5X, 65HTIME VERSUS HEAD AND CONCENTRATION AT SELECTED O
BSERVATION POINTS//15X, 1HPUMPING PERIOD NO. , 14///)
410 FORMAT (1H0, 16X, 19HTRANSIENT SOLUTION///)
420 FORMAT (1H0, 15X, 21HSTEADY-STATE SOLUTION///)
FORMAT (1H0,20X,22HOBS.WELL NO. X Y,17X,1HN,6X,40HHEAD (FT)
     1 CONC.(MG/L) TIME (YEARS) /24X,I3,9X,I2,3X,I2//)
FORMAT (1H ,3X,45H** NOTE ** THIS OBS. WELL IS LOCATED OUTSIDE/16
     1X,24HOF THE TRANSPORT SUBGRID)
FORMAT (1H ,58X,I2,6X,F7.1,8X,F7.1,8X,F7.3)
FORMAT (1H ,2X,21HCHEM.TIME(SECONDS) = ,E12.5)
FORMAT (1H ,2X,21HCHEM.TIME(YEARS) = ,E12.5)
FORMAT (1X,2I2,I5)
END
ASMOD

SUBROUTINE ASMOD

include params

REAL *8TMX, VPRM, HI, HR, HC, HK, WT, REC, RECH, TIM, AOPT, TITLE
REAL *8XDEL, YDEL, S, AREA, SUMT, RHO, PARAM, TEST, TOL, PINT, HMIN, PYR
REAL *8FCTR, TIMX, TINIT, PISS, YNS, XNS, RAT, HMx, HMY
REAL *8TNSUM, ANTIM, TDEL
REAL *8DXINV, DXINV, ARINV, POFINV
REAL *8TINT, ALPHAL, ANITP
REAL *8CW, CWL, THETA, THETA, ASG, ASD, EOM, MLT
REAL *8TAU, TAUFL, TAU, FORV, TAUN, DCMAX, DCMAXN, DLMAX
REAL *8MASS, BMAS, BMASS, BMASS, CONST, RMSAX, DLTC
REAL *8RCW, RCWL, RTHO, RTHW, G, D

INTEGER RSCMPS, IOUT

COMMON /PRM/ NTIM, NMP, NPNT, NTP, N, NX, NY, NP, NREC, INT, NNX, NNY, NUMO
1BS, NMOV, IMOV, NMAX, ITMAX, NZCRIT, IPRNT, NPTPND, NPNTMV, NPNTVI, NPNTD, N
2PNCHV, NPDEL, ICNK, IN
COMMON /PRMC/ NODEID(ZX, ZY), NPCELL(ZX, ZY), NPOLD(ZX, ZY), LIMBO(500),
1XOBS (5), YOBS (5)
COMMON /HEDB/ TMRX(ZX, ZY, Z), VPRM(ZX, ZY), HI(ZX, ZY), HR(ZX, ZY), HC(ZX,
1ZY), HK(ZX, ZY), HT(ZX, ZY), REC(ZX, ZY), RECH(ZX, ZY), TIM(100), AOPT(20),
2TITLE(10), XDEL, YDEL, S, AREA, SUMT, RHO, PARAM, TEST, TOL, PINT, HMIN, PYR
COMMON /CHMA/ PART(3, 2F), CONC(ZX, ZY), TMCHN(5, 50), VX(ZX, ZY), VY(ZX,
1, ZY), CMINT(ZX, ZY), CNRECH(ZX, ZY), MY, SUMCH, BETA, TIMV, STORM, STOR
2MI, CVSIN, CVMSOUT, FLMIN, FLMOT, SUMO, CELDIS, DLTRAT, STORM
COMMON /RSC/ CWL(NCP), CWL(NCP), THETA, THETAR(NCP), ASG, ASD
1, NCP, EOM(ZX, ZY), TAU(ZX, ZY), MLT(ZX, ZY), RSCMPS, RMSAX, DLTC

************************************************************************************
SAVE

TAUFL = 0.0
TAUL = 0.0
FORV = 0.0
AMASS = 0.0
CONST = 0.0
BMASS1 = 0.0
BMASS2 = 0.0
BMAS = 0.0
IOUT = 1

WRITE(2, 1270)
DO 20 IY = 1, NY
   DO 30 IX = 1, NX
      IF (EOX(IX, IY) .EQ. 0.0) GO TO 30
      RECH(IX, IY) = RECH(IX, IY) * MLT(IX, IY)
      DLMAX = 0.0
   30 CONTINUE
20 CONTINUE

DO 40 IJ = 1, RSCMPS
RCWI = CWI(IJ)
RCWL = CWL(IJ)
RTHO = THETAQ(IJ)
RTHW = THETAW(IJ)
G = ASG(IJ)
D = ASD(IJ)
TAUN = 0.0
DCMASS = 0.0
DCMASSN = 0.0

TAUPL = 1.0 + (RTHO/RTHW*G*D*RCWI**(D-1.0))
TAUL = 1.0 + (RTHO/RTHW*G*D*RCWL**(D-1.0))
PORV = ECM(IX,IY) * RTHW * AREA
AMASS = RCWI * TAUPL * PORV
CONST = (RTHW/(RTHO*G*D))**(1.0/(D-1.0)) * PORV
BMASS1 = CONST * (D-1.0)/D * (TAUPL - 1.0)**(D/(D-1.0))
BMASS2 = CONST * (D-1.0)/D * (TAUL - 1.0)**(D/(D-1.0))
BMASS = BMASS2 - BMASS1

IF (TAU(IX,IY) .LE. TAUPL) THEN
  DCMASS = TAU(IX,IY) * RCWI * PORV
ELSE
  IF (TAU(IX,IY) .GE. TAUL) THEN
    DCMASS = AMASS + BMASS + (TAU(IX,IY)-TAUL)*RCWL*PORV
  ELSE
    DCMASS = AMASS + (CONST*(D-1.0)/D*
    (TAU(IX,IY)-1.0)**(D/(D-1.0)) - BMASS1)
  ENDIF
ENDIF

TAUN = TAU(IX,IY) + (TIMV)*(-RECH(IX,IY)*AREA/PORV)
IF (TAUN .LE. TAUPL) THEN
  DCMASSN = TAUN * RCWI * PORV
ELSE
  IF (TAUN .GE. TAUL) THEN
    DCMASSN = AMASS + BMASS + (TAUN-TAUL)*RCWL*PORV
  ELSE
    DCMASSN = AMASS + (CONST*(D-1.0)/D*
    (TAUN-1.0)**(D/(D-1.0)) - BMASS1)
  ENDIF
ENDIF

DLMASS = DLMASS + (DCMASN - DCMASS)
CONTINUE

CNRECH(IX,IY) = DLMASS / (-RECH(IX,IY)*AREA*TIMV))
WRITE(2,1250) TAU(IX,IY), TAUN, IX, IY, CNRECH(IX,IY)

IF (IOUT.EQ.1) THEN
  T1 = SUMTCH / (86400.0*365.25)
  T2 = (SUMTCH+TIMV) / (86400.0*365.25)
  WRITE(15,1300) TAU(IX,IY), CHAR(9), T1, CHAR(9), CNRECH(IX,IY)
  WRITE(15,1300) TAUN, CHAR(9), T2, CHAR(9), CNRECH(IX,IY)
ENDIF
IOUT = IOUT + 1
TAU(IX, IY) = TAUN
RECH(IX, IY) = RECH(IX, IY) / MLT(IX, IY)
CNRECH(IX, IY) = CNRECH(IX, IY) * MLT(IX, IY)
RSMASS = RSMASS + DLMASS

C
30 CONTINUE
20 CONTINUE
RETURN
1250 FORMAT (1H, 16X, 'FROM TAU = ', E10.4, ' TO ', E10.4,
1', CNRECH(', I2, ', ', I2, ') = ', F10.4)
1270 FORMAT (/1H, 11X, '** THE FOLLOWING ASSIGNMENTS HAVE BEEN'
1', ' MADE FOR A RESIDUAL SOURCE: /)
1300 FORMAT (E10.4, A1, E10.4, A1, E10.4)
END
List of References


