MODEL UNCERTAINTY AND PARAMETER SENSITIVITY IN LINEAR RETARDANCE FORMULATIONS

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ABSTRACT

Preliminary sensitivity and uncertainty analyses were performed to examine the effects of adsorption parameter and model selection on solute transport. It was found that while sensitivity increased with increasing retardation factor (R), local maximums existed for specific mass transfer coefficients. Comparisons between the concentrations predicted by equilibrium and non-equilibrium models showed that in the time period $0 < T \leq R$, the traditional equilibrium model always under-predicted the concentration simulated by non-equilibrium assumptions. A maximum possible error of -100 percent existed. For the time $T > 2R$, however, the equilibrium assumption always over-predicted the concentration with a maximum possible error of +25 percent. For the time $R < T \leq 2R$, the equilibrium may either under- or over-predict the output concentration, with a possible error ranging from -50 to +25 percent. The discrepancies between equilibrium and non-equilibrium models increased rapidly as the mass transfer coefficient decreased. This indicated that significant errors may result from using equilibrium transport model to simulate solutes undergoing non-equilibrium adsorption, especially for hydrophilic compounds where mass transfer rate are slow.

INTRODUCTION

Recent developments in groundwater transport modeling have been aided by a combination of an increased understanding of fundamental transport mechanisms as well as the increasing availability of computers. Groundwater transport models have been routinely used by regulatory agencies and consulting firms to address management issues and assist in decision making. However, this ever increasing use of models has raised concerns as to uncertainties associated with their abilities to simulate real world pollution problems. These uncertainties have become an additional important factor in performing risk assessments for groundwater contamination problems [1]. Accurate simulation depends upon such factors as the appropriate description of pertinent transport mechanisms, the proper choice of transport codes and the use of accurate input parameters.

Two types of uncertainties may impact the simulation process: those associated with model selection and those related to parameter identification. Model uncertainty results from the improper description of the transport mechanisms, or by applying the model to situations unwarranted by its formulation. Parameter uncertainty occurs when inaccurate or improper input values are used. Model and parameter uncertainties have been classified as type I and type II errors respectively [2], and both have been shown to affect the reliability of the simulation.

For groundwater contaminant transport problems, these uncertainties tend to become more obvious when complex transport mechanisms are involved and are exacerbated by the difficulties in obtaining accurate and consistent input data. The discrepancies between the prediction and underlying monitoring data due to improper model selection or to uncertain input data can make the results unusable. Villeneuve et al. found that for the unsaturated zone transport model, PRZM, a variation of 15 to 22 percent in the degradation constant, or a 24 percent variation in the adsorption constant, could lead to 100 percent uncertainty of the output pesticide concentration [3].

Recently, uncertainty analysis has become a major research topic and a considerable amount of work has been published. Burges et al. first applied basic uncertainty theory to stream water quality evaluations [2]. Subsequent applications have also been found in groundwater determinations. Loague et al. assessed the impact of uncertainty in soil, meteorological and chemical properties on pesticide leaching [4]. Medina et al. employed sensitivity and Monte Carlo techniques to analyze the uncertainties associated with the impact of waste sites on groundwater quality [5], while Villeneuve et al. investigated parameter sensitivity for the unsaturated root zone model (PRZM) [3]. While these efforts primarily employed first order or Monte Carlo methods to analyze parameter uncertainty, model uncertainty has attracted less attention. This article attempts a preliminary assessment in this area within the context of parameter selection. This work primarily focused on the sensitivity of different parameters and the possible errors resulting from model selection. Specifically, the interactions between equilibrium

and non-equilibrium linear adsorption with attendant parameter selection were investigated.

The deterministic model used for these purposes was developed by Chen and McTernan [6]. This Multi-substrate, Multi-option Groundwater Transport Model (MMGTM) consists of various sub-models and can simulate the transport of two substrates and oxygen under various conditions including advection, dispersion, adsorption, and biological decay. Adsorption and biological decay options available to the user include equilibrium or non-equilibrium adsorption with Linear, Langmuir, or Freundlich isotherms as well as Monod or first order biological decay.

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

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

(1)

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

$$q = \frac{m_x}{M} = k_d C$$

(2)

and indicates that solute concentration in the solid phase is proportional to the concentration in the liquid phase. The adsorption of a number of organics onto soil at low concentration has been reported to be linear and served as a starting point for this analysis [7, 8].

Applying the differential train rule and combining with Equation (2):

$$\frac{\partial q}{\partial t} = \frac{\partial q}{\partial C} \frac{\partial C}{\partial t}$$

(3)

$$\frac{\partial q}{\partial C} = K_d$$

(4)

and substituting Equations (3) and (4) into Equation (1):

$$R \frac{\partial C}{\partial t} = -U \frac{\partial C}{\partial x} = D \frac{\partial^2 C}{\partial x^2},$$

(5)

where

$$R = 1 + \frac{\rho_b K_d}{\varepsilon}$$

(6)

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

The above process assumes an *equilibrium* always exists between the liquid and solid phases, and is defined by Equation (4). This assumption is valid only if the transfer of mass from liquid phase to the solid is instantaneous. Adsorption, in fact, is a time dependent mass transfer process where the equilibrium assumption may be used only if the mass transfer rate is fast relative to the groundwater velocity. Many current groundwater transport codes employ equilibrium or retardance approaches to simulate contaminant transport and a great deal of work has focused on determination of Kd or retardation factor. Several methods have been developed for the determination of these values, including lab batch adsorption tests, field tracer measurements as well as soil organic content correlations. However, all of these efforts have been based upon the linear, equilibrium assumption. While acceptable in some circumstances, this has been shown to be deficient in others [9, 10]. Selection of a retardation based approach to simulate these types of conditions will introduce much uncertainty and resultant error in the final output.

If the mass transfer process is slow, however, an equilibrium assumption may become inappropriate and a kinetically based approach is more fundamentally valid. Such conditions could occur with specific hydrophilic chemicals or when hydraulic conditions are altered during remediation. One approach to describe this process is by the internal resistance model, provided by Hines and Maddox [11]:

$$\frac{\partial q}{\partial t} = k_s A_s (q* - q) .$$

(7)

Here, an overall mass transfer coefficient, r, may be used to represent K_s and A_s:

$$r = k_s A_s .$$

(8)

Equation (7) becomes:

$$\frac{\partial q}{\partial t} = r(q* - q) .$$

(9)

Substitution into Equation (1) yields:

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

(10)

Particular to adsorption, model uncertainty results from the selection of either \equilibrium or non-equilibrium algorithms while parameter uncertainty in selecting either the distribution coefficient Kd or an overall mass transfer coefficient r can also reduce accuracy. The variation in Kd may come from many sources: the

heterogeneity of the aquifer materials, the uneven distribution of organic materials, variation in temperature, error from field and lab measurements or from regression models used to correlate chemical and geological data. In addition to these factors, the surface area of aquifer materials and the groundwater velocity also have important impacts on the overall mass transfer coefficient r. This article investigated the impact of variability of parameters K_d and r on the model output, as well as their effects on the model uncertainty.

METHODOLOGY

Data Transformation

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

Dimensionless Time

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

Dimensionless Concentration

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

Imaginary Distribution Coefficient and Retardation Factor

For non-equilibrium adsorption, the distribution coefficient Kd describing equilibrium conditions was not appropriate, as the molecular distribution between the aqueous and solid phases defined by equilibrium was not achieved. To address this, an imaginary distribution coefficient, Ki, could be defined as a reference state for a

quasi-equilibrium adsorption level, assuming no mass transfer resistances would exist. In the simulation process, K_i defined the reference solid phase concentration q^*, which determined the overall mass transfer rate (Equation (9)). Similarly, a corresponding imaginary retardation factor, R_j, was calculated by Equation (6).

Input Data

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

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

The distribution coefficient, K_d, and the overall mass transfer coefficient r were varied in the sensitivity analysis with values for K_d ranging from zero (no adsorption) to 1.1 cm^3/gm, with a corresponding range of retardation factor from 1 to 4.3. This K_d range was selected to address typical values for a number of pesticides and halogenated organics in soil and aquifer materials [12, 13]. The range of overall mass transfer coefficients chosen for this analysis was from zero to a value that resulted in an equivalent equilibrium condition, where further increase of the value did not change the resultant output. A summary of input data used in this analysis is shown in Table 1.

Table 1. Input Parameters Used in Analysis

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

Sensitivity Analysis

Sensitivity analysis deals with the response of change of model output to the change of input parameters. The coefficient of sensitivity S has been expressed previously by Sykes et al. [14] as :

$$S = \frac{\partial P/P}{\partial \alpha/\alpha},$$

(11)

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

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

Analysis of Mean Error

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

$$E_m = \sqrt{\frac{\sum_{i=1}^{20} (Ce_i - Cn_i)^2}{20}}.$$

(12)

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

RESULTS

Effects of Retardation Factor

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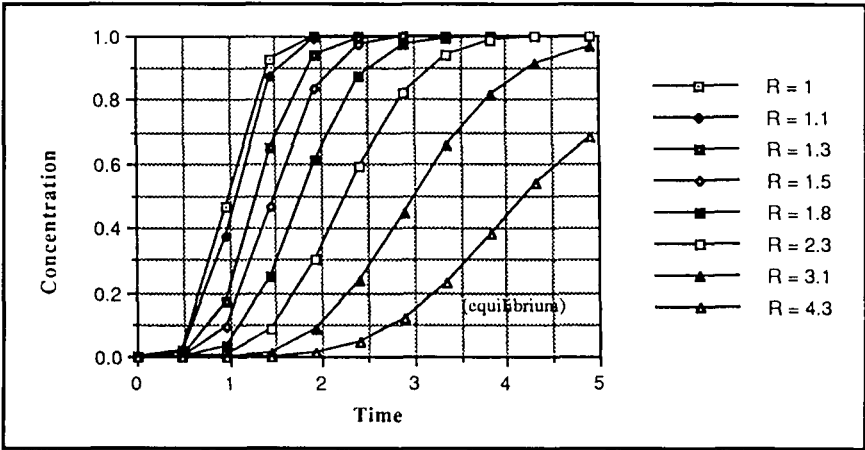

Figure 1. Effect of retardation on breakthrough curves
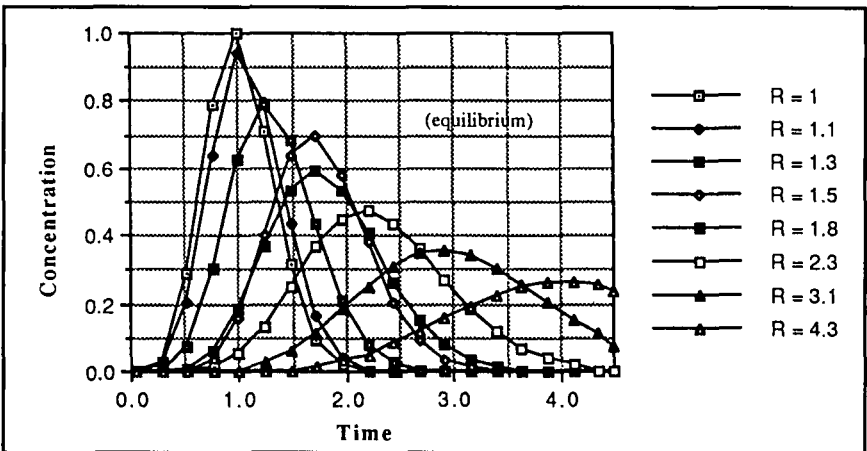(continuous boundary input).

Figure 2. Effect of retardation on breakthrough curves
(pulse boundary input).

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

Effects of Overall Mass Transfer Coefficient

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

The comparison of non-equilibrium and equilibrium breakthrough curves with equivalent K_i or R_i can be seen in Figure 3. When the mass transfer coefficient was equal to zero, the breakthrough curve overlapped the curve resulting from the no-adsorption option (i.e., advective-dispersive). As the magnitude of the mass transfer coefficient increased, the breakthrough curve tended to approach the curve resulting from equilibrium adsorption with equal K_d or R values. Selection
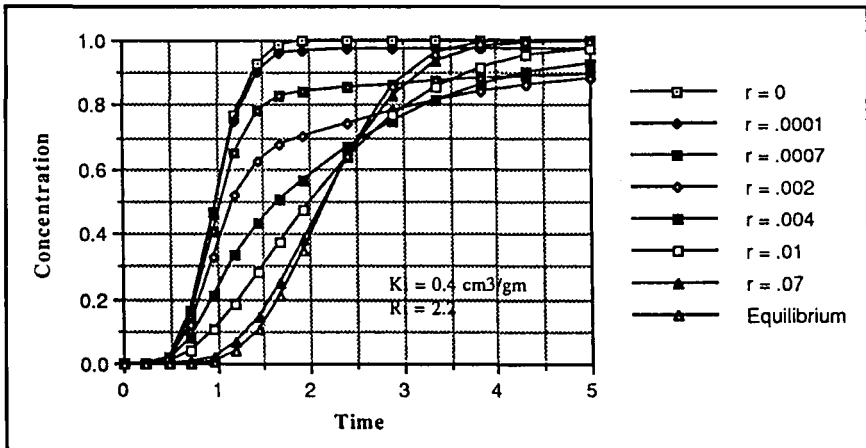

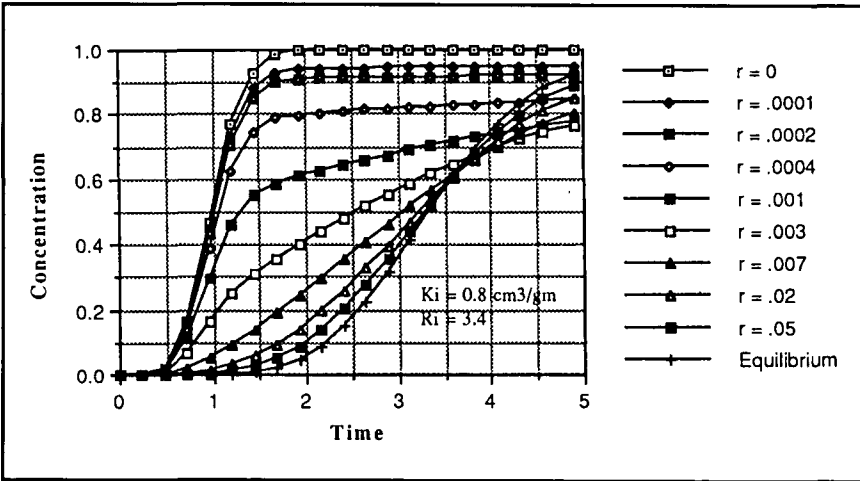Figure 3. Effect of mass transfer coefficient on breakthrough curves (continuous boundary input. R_i = 2.2).

Figure 4. Effect of mass transfer coefficient on breakthrough curves (continuous boundary input. $R_i = 4.3$).

of either zero or a large mass transfer coefficient resulted in a 100 percent breakthrough of concentration with increased time. However, asymmetrical curves with prolonged, less than total breakthrough tails were observed for an intermediate range of r. The equilibrium assumption may either over or under estimate the simulated concentration, depending upon the time at which the concentration was observed. Figure 4 presents similar comparisons for a larger R_i. The greater R_i transferred the equilibrium curve farther along the temporal axis, while the curve for r equal to zero overlapped that from no adsorption, as with the previous case. Zero mass transfer reduces transport to the advective-dispersive portion of Equation (1), while at higher mass transfer coefficient values, equilibrium is approximated.

Figure 5 shows the effect of mass transfer coefficient selection on breakthrough curves under non-equilibrium, pulsed boundary input conditions. As with the continuous boundary examples, the breakthrough curve for r equal to zero coincided with the advective-dispersive case. As r increased, the concentration peaks decreased and appeared at increased time until r reached 0.011. As r further increased, the peak began to increase and approached equilibrium adsorption. The breakthrough curves for no or equilibrium adsorption were symmetrically shaped with zero concentration at both ends. However, asymmetrical breakthrough curves with non-zero concentration tails were observed for non-equilibrium adsorption over a range of mass transfer coefficients. Figure 6 illustrated the similar effect with a larger value of Ri (Ri = 3.4). In this situation, the curve for r equal to zero again overlapped the advective-dispersive condition, as shown in Figure 5.
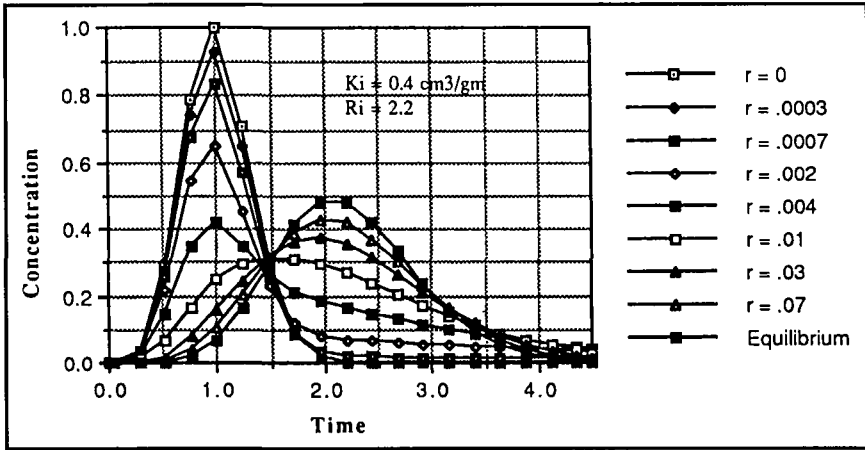
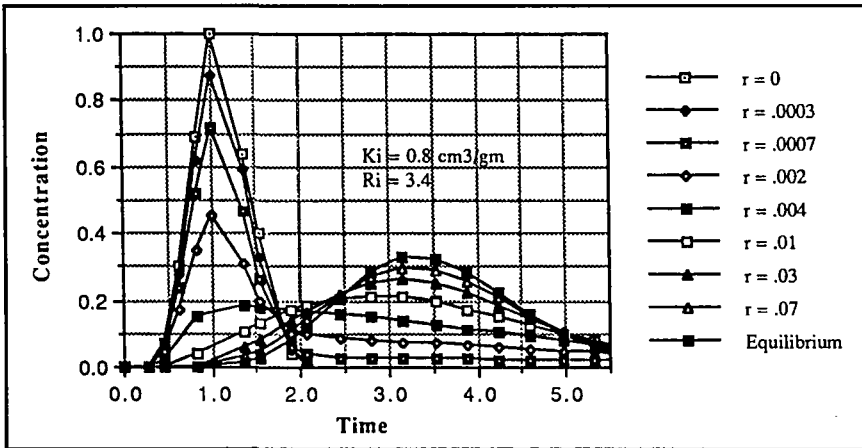Figure 5. Effect of mass transfer coefficient on breakthrough curves (pulse boundary boundary input. R_i = 2.2).

Figure 6. Effect of mass transfer coefficient on breakthrough curves (pulse boundary boundary input. R_i = 3.4).

Sensitivity of Retardation Factor and Mass Transfer Coefficient

Sensitivity analysis was applied to the retardation factor and overall mass transfer coefficient for equilibrium and non-equilibrium conditions respectively. Figure 7 presents the sensitivity for retardation factor R in an equilibrium situation for continous injection of contaminant at the aquifer boundary. For any value of retardation factor, the sensitivity was always negative, indicating that the solute
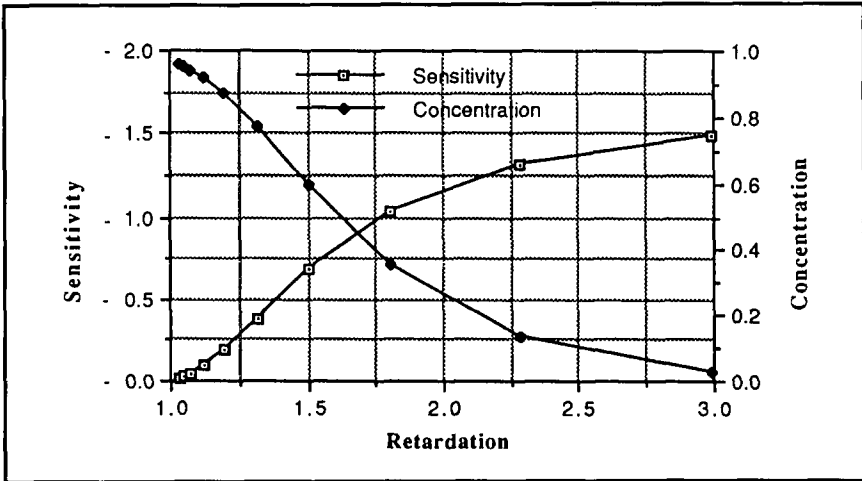
Figure 7. Sensitivity and output concentration as a function of retardation factor (at T = 1.6).

concentration, as expected, would decrease as R increased. The magnitude of sensitivity increased as R increased, indicating that selection of higher values of R resulted in greater sensitivity. Although Figure 7 was generated at time equal to 1.6, the general effect was similar at other times. This can be observed by examining the breakthrough curves in Figure 1.

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

A typical curve representing time T > R is illustrated in Figure 9. In this case not only the magnitude of sensitivity varied with r, but the sign also changed. Two sensitivity peaks were generated, one positive and the other negative. The opposite signs indicated different directions of response of output concentration to the input parameter. The concentration curve in the figure showed that as r increased over the range 0.0001 to 0.00105, the output concentration decreased from 0.97 to 0.88. But as r continued to increase from 0.00105 the breakthrough concentration began to increase and approached 1 when r equaled 0.1. Accompanying sensitivity cycled from maximum negative values through peak positive response to asymptote to approximate zero above r = 0.1.
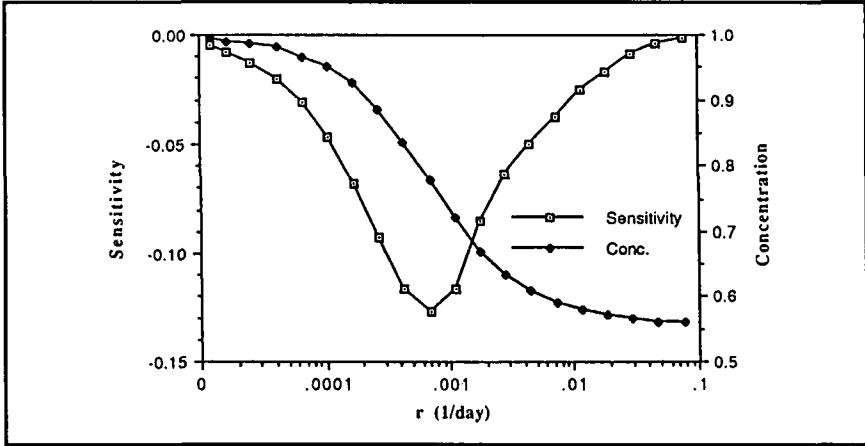
Figure 8. Sensitivity and output concentration as a function of mass transfer coefficient (continuous boundary input, T = 0.94 R).

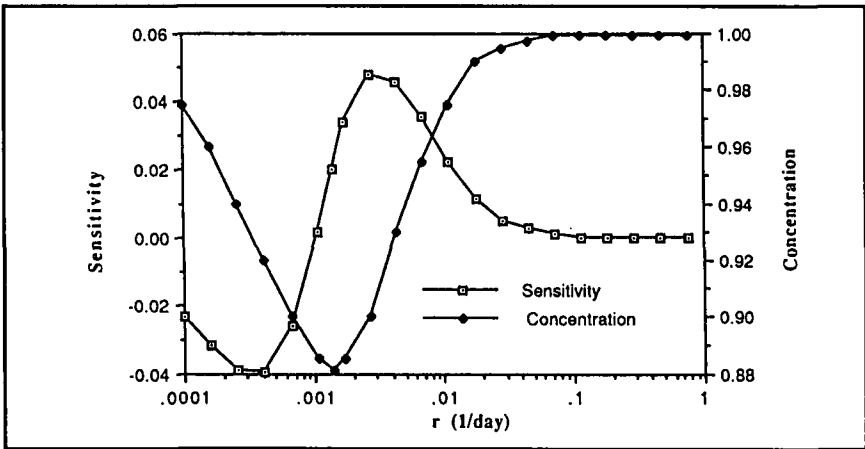Figure 9. Sensitivity and output concentration as a function of mass transfer coefficient (continuous boundary input, T = 2.2 R).

Uncertainties for Parameters and Models

The possible errors introduced by applying an equilibrium model to non-equilibrium situations are presented in Figure 10, where the error in ordinate represents the difference between the concentrations predicted from equilibrium and non-equilibrium models, respectively. Time was expressed as multiples of the retardation factor. To locate the specific time, a conversion of time into the
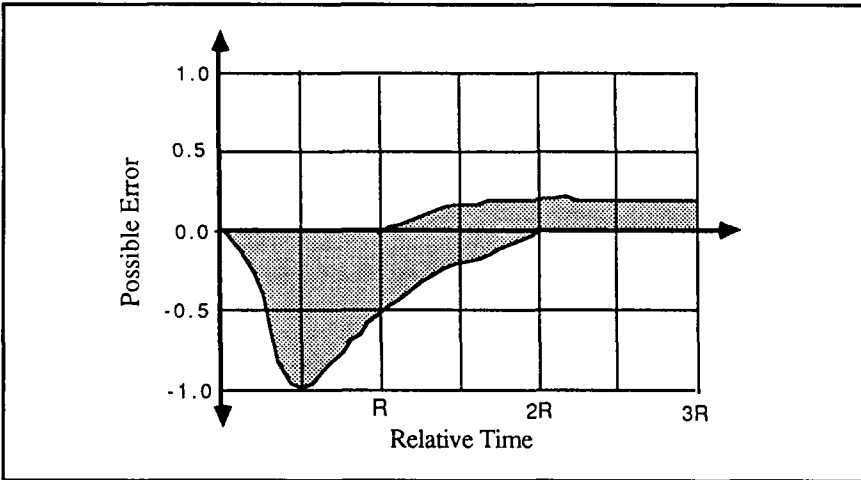
Figure 10. Possible error resulted from assumption of equilibrium adsorption.

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

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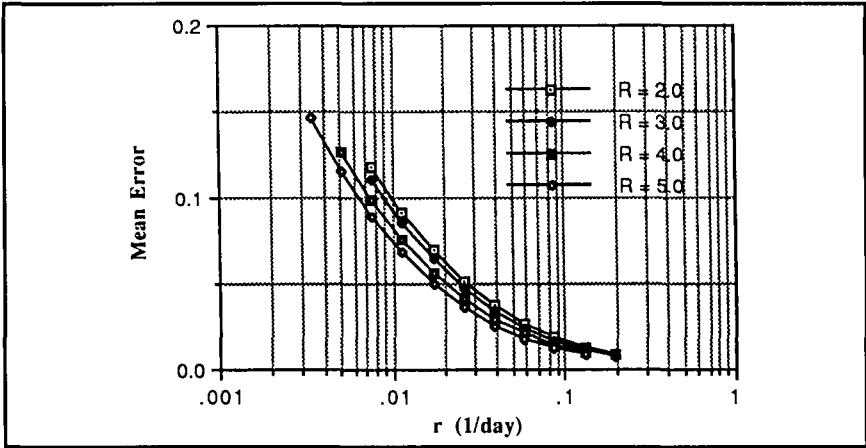
Figure 11. Mean error resulting from equilibrium assumption as a function of mass transfer coefficient (continuous boundary input).
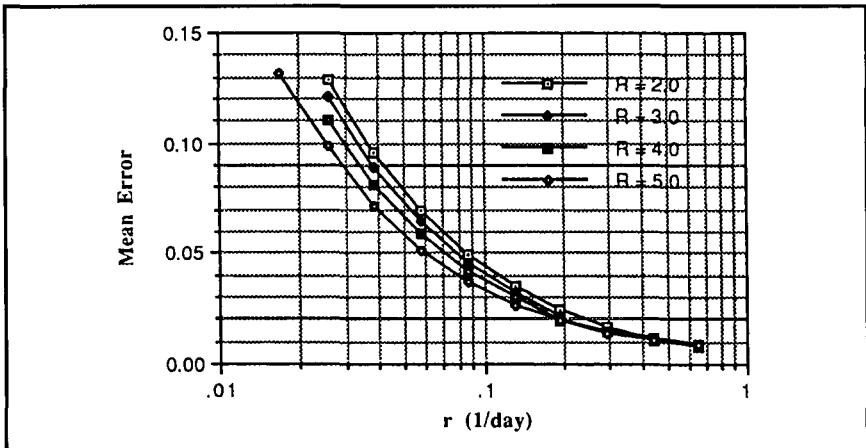

Figure 12. Mean error resulting from equilibrium assumption as a function of mass transfer coefficient (pulse boundary input).

DISCUSSION

The selection of retardation factors caused a variation of contaminant arrival time and intermediate concentrations for the continuous boundary condition. It did not, however, attenuate the final concentration which was always equal to the boundary's value. For the pulsed boundary input, however, an over estimate of R not only resulted in a delayed arrival of contaminant but also generated a reduced

peak concentration. When application to groundwater remediation practice is considered, the uncertainty in R may affect the prediction as to whether a maximum allowable concentration would be violated and, if so, when this violation would occur. The magnitude of uncertainty can be seen in Figure 7, where a maximum sensitivity coefficient of 1.5 was observed corresponding to R = 30. This value of sensitivity coefficient indicated that 66.7 percent uncertainty in R would result in 100 percent uncertainty in the predicted concentration. The increased sensitivity with increased R also indicated that an over estimated R posed not only a potential risk for under prediction of concentration but also resulted in greater uncertainty for the prediction.

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

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

The evaluation of uncertainty from improper use of an equilibrium model for non-equilibrium situations can be preliminarily identified by employing Figure 10, with a simple transformation. For example, if one wants to estimate the error from the prediction of 400 day's concentration by improperly using an equilibrium model for non-equilibrium situations, the time should be first transformed

to dimensionless units. Assuming a dimensionless time of 0.8 is obtained from given physical conditions, and the retardation used for the equilibrium simulation is 4.0, then the time expressed as multiple of retardation factor becomes 0.8/4.0 = 0.2R. Using this value in Figure 10, the error range is 0 to -0.4. This means for any possible value of mass transfer coefficient, the maximum error could not be greater than 40 percent. The actual error would fall between 0 and 40 percent, depending upon the value of mass transfer coefficient selected.

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

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

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

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

Given the same value of mass transfer coefficient, a slightly smaller error was observed for a greater value of retardation factor, but this effect appeared minimal. The main error was due to the selection of mass transfer coefficient. For a retardation factor of 2.0 and continuous boundary input condition, the error from improper use of the equilibrium model would be less than 5 percent if the overall mass transfer coefficient was greater than 0.025/day. A larger error was observed for pulsed boundary input conditions, with the same retardation factor and mass

transfer coefficient. In both continuous and pulsed boundary input conditions, a rapid increase in error occurred as the mass transfer coefficient decreased. The larger expected error associated with smaller mass transfer coefficient selection signified the inability of the equilibrium model to simulate non-equilibrium situations, especially when slow mass transfer dominated the adsorption process. These situations tended to occur when hydrophilic compounds were present and hydraulic contact time was limited. The results from Figures 11 and 12 can also be used for general error estimations for situations where the equilibrium model has been used to simulate non-equilibrium adsorption.

SUMMARY AND CONCLUSIONS

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

While the sensitivity of the retardation factor showed similar results to other research work [3], the sensitivity resulting from the selection of the mass transfer coefficient exhibited different and more complicated patterns. These included the local maximums of sensitivity for specific r values and sign changes at different observation times. These properties demonstrated a higher degree of uncertainty when non-equilibrium adsorption dominated.

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

NOMENCLATURE

A_s = Specific area of adsorptive medium, L^{-1}
C = Aqueous phase substrate concentration, ML^{-3}
Ce = Normalized output substrate concentration for equilibrium adsorption, dimensionless

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

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

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

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

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

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

m = Mass of adsorptive medium, M

m_x = Mass of adsorbed solute, M

P = Value of output data in sensitivity analysis

q = Solid phase substrate concentration, dimensionless

q^* = Equilibrated solid phase substrate concentration, dimensionless

R = Retardation factor, dimensionless

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

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

S = Coefficient of sensitivity, dimensionless

T = Dimensionless time, dimensionless

t = Time, T

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

x = Distance, L

α = Value of input data in sensitivity analysis

ε = Porosity of adsorptive medium, dimensionless

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

REFERENCES

1. Y. Y. Haimes, Risk Assessment for the Prevention of Groundwater Contamination, in *Groundwater Contamination (Studies in Geophysics)*, National Academy Press, Washington, D.C., 1984.

2. S. J. Burges and D. P. Lettenmaier, Probabilistic Methods in Stream Quality Management, *Water Resources Bulletin, 11*:1, pp. 115-130, 1975.

3. J. P. Villeneuve, P. Lafrance, O. Banton, P. Frechette, and C. Robert, A Sensitivity Analysis of Adsorption and Degradation Parameters in the Modeling of Pesticide Transport in Soils, *Journal of Contaminant Hydrology, 3*, pp. 77-96, 1988.

4. K. Loague, R. E. Green, T. W. Giambelluca, T. C. Liang, and R. Yost, Impact of Uncertainty in Soil, Climatic and Chemical Information in a Pesticide Leaching Assessment, *Journal of Contaminant Hydrology, 5*, pp. 171-194, 1990.

5. M. A. Medina, Jr., J. B. Butcher, and C. M. Marin, Monte Carlo Analysis and Bayesian Decision Theory for Assessing the Effects of Waste Sites on Groundwater, II: Applications, *Journal of Contaminant Hydrology, 5*, pp. 15-31, 1989.

6. Z. Chen and W. F. McTernan, Multi-Substrate, Multi-Option Groundwater Transport Model, paper accepted for publication in *Journal of Contaminant Hydrology*, 1992.
7. J. C. Means, S. G. Wood, J. J. Hassett, and W. L. Banwart, Sorption of Polynuclear Aromatic Hydrocarbons by Sediments and Soils, *Environmental Science and Technology*, *14*:12, pp. 1524-1528, 1980.
8. J. J. Hasset, J. C. Means, W. L. Banwart, S. G. Wood, S. Ai, and A. Khan, Sorption of Dibenzothiophene by Soils and Sediments, *Journal of Environmental Quality, 9*, pp. 184-186, 1980.
9. R. A. Freeze and J. A. Cherry, *Ground Water*, Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1979.
10. Z. Chen, W. F. McTernan, and A. L. Hines, A Preliminary Investigation into the Mass Transfer Properties of a Pesticide onto Abiotic Media, *Journal of Environmental Systems, 20*:3, pp. 91-109, 1990-1991.
11. A. L. Hines and R. N. Maddox, *Mass Transfer – Fundamentals and Applications*, Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1985.
12. H. Siegrist and P. L. McCarty, Column Methodologies for Determining Sorption and Biotransformation Potential for Chlorinated Aliphatic Compounds in Aquifers, *Journal of Contaminant Hydrology, 2*, pp. 31-50, 1987.
13. W. Z. Zhong, A. T. Lemley, and R. J. Wagenet, Quantifying Pesticide Adsorption and Degradation during Transport through Soil to Groundwater, in *Evaluation of Pesticides in Ground Water*, W. Y. Garner, R. C. Honeycutt, and H. N. Nigg (eds.), American Chemical Society, Symposium Series, 315, pp. 61-77, 1986.
14. J. F. Sykes, J. L. Wilson, and R. W. Andrew, Sensitivity Analysis for Steady-State Groundwater Flow Using Adjoin Operators, *Water Resources Research, 21*:3, pp. 359-371, 1985.

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