

Hybrid-Cells-in-Series Model Incorporating Adsorption for Solute Transport in a Stream

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ABSTRACT: Most trace elements and many anthropogenic organic compounds are known to associate with sediments. Adsorption and desorption take place under non-equilibrium conditions. Coupling the non-equilibrium adsorption kinetics with the primary mechanisms of advection-dispersion, the hybrid cells in series model (HCIS), an alternate to the classical Advection-Dispersion Equation (ADE) model, is extended to determine concentration of a solute downstream of a point source of pollution. The HCIS model is a conceptualized model, comprising of a plug flow zone and two thoroughly mixed unequal reservoirs, all connected in series, converts the transport process governed by the second order partial differential equation with space ordinate and time as independent variables to an equivalent process governed by a first order total differential equation with time as independent variable there by greatly simplifying the solution technique. Using the non-equilibrium Freundlich type adsorption isotherm, and unit pulse kernel coefficients, and applying convolution technique, temporal and spatial solute concentrations downstream of an injection point is simulated.

INTRODUCTION

Various processes in addition to primary mechanisms of advection-dispersion determine the fate and transport of solutes in streams. One such important process controlling the concentrations of solutes in streams is adsorption and desorption to and from bed sediments below the water column. Many investigators (Deacon and Driver, 1999; Jain and Sharma, 2002; Perk *et al.*, 2006) have reported strong association of numerous toxic chemicals both organic and inorganic - with sediments below water column in streams. The association of chemicals and inorganic contaminants with sediment means that much of the downstream transport of these materials cannot be detected or evaluated solely through the sampling and analysis of water because of non-equilibrium sorption isotherms of solutes between the water column and the streambed. Thus, the need of development of a predictive model coupling the physical processes of adsorption with the primary mechanism of solute transport has been arisen.

Many investigators have reported limitations (Day, 1975; Chatwin, 1980; Chatwin and Allen, 1985) in

application of the classical Advection Dispersion Equation (ADE) model (Taylor, 1954) to natural streams. An alternate to the ADE model, a conceptual hybrid-cells-in-series (HCIS) model comprised of: (i) a plug flow zone, and (ii) two thoroughly reservoirs of unequal residence time all connected in series (Ghosh *et al.*, 2004) is shown in Figure 1. The physical processes of transport of solutes representing advection and dispersion in a unit of the HCIS model are described by three time parameters: α , the residence time of solute in the plug flow zone, T_1 , the residence time of solute in the first reservoir, and T_2 , the residence time of solute in the second reservoir. The parameter α characterizes pure advection and the other two parameters T_1 and T_2 characterize dispersion and advection. Under steady and uniform flow conditions, when the linear size of the hybrid unit, Δx , is more than or equal to $4 D_L/u$, where D_L is the longitudinal dispersion coefficient and u is the mean flow velocity, the concentrations simulated by the HCIS model at $n\Delta x$, $n = 1, 2, 3 \dots$ are nearly equal to the analytical solution of the advection-dispersion equation model.

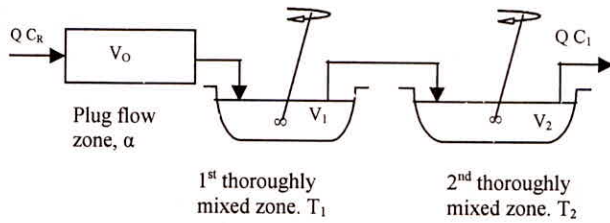


Fig. 1: The First Process Unit of the HCIS Model

In this paper, using a simplified non-equilibrium adsorption isotherm, the HCIS model has been extended to simulate solute transport when adsorption takes place in the plug flow zone as well as in the thoroughly mixed zones.

MODEL FORMULATION

The non-equilibrium Freundlich type adsorption isotherm as given by Bear and Bachmat (1990) is,

$$\frac{dC_s(t)}{dt} = R_d [C(t) - C_s(t)] \quad \dots (1)$$

in which $C_s(t)$ is the mass adsorbed per unit wetted surface area (Wp) of the river i.e., if the mass absorbed up to time 't' per unit surface area is put in a unit volume of the solvent (water), the solute will have a concentration equal to $C_s(t)$; $C(t)$ is the concentration of solute in the river; and R_d is the proportionality constant.

In a thoroughly mixed reservoir, adsorption varies only with time but within the plug flow zone, the time of contact of the incoming solute with the wetted perimeter will vary from section to section. Therefore, the quantity absorbed on the wetted surface, besides varying with time, would also vary along the plug flow zone. Consequently, the average concentrations of the solute in vertical water columns within the plug flow zone will vary from column to column. The differential Eqn. 1 is first solved for constant 'C' and the expression for $C_s(t)$ for time varying concentration 'C(t)' is then derived using a convolution technique. For an initial condition $C_s(t) = 0$, the solution for constant 'C' is,

$$C_s(t) = C [1 - e^{-R_d t}] \quad \dots (2)$$

For $C = 1$, the expression in Eqn. 2 can be regarded as unit step response function. Its differential with time would give the unit impulse response function. For time varying 'C(t)', the expression for $C_s(t)$ is given by,

$$C_s(t) = R_d \int_0^t C(\tau) e^{-R_d(t-\tau)} d\tau \quad \dots (3)$$

in which τ is a dummy variable. Discretizing the time span with uniform time step size ' Δt ' and assuming

that within a time step $C(t)$ is constant but it varies from step to step, Eqn. (3) can be written as,

$$C_s(n\Delta t) = \sum_{\gamma=1}^n \left\{ \left(\frac{C((\gamma-1)\Delta t) + C(\gamma\Delta t)}{2} \right) \left[e^{-R_d \Delta t(n-\gamma)} - e^{-R_d \Delta t(n-\gamma+1)} \right] \right\} \quad \dots (4)$$

where n is an integer.

Let a discrete kernels $\delta_s(m)$ be defined as,

$$\delta_s(m) = R_d \int_0^{\Delta t} e^{-R_d(m\Delta t-\tau)} d\tau = e^{-R_d \Delta t(m-1)} - e^{-R_d \Delta t m}$$

where m is an integer. Eqn. (4) can be rewritten as,

$$C_s(n\Delta t) = \sum_{\gamma=1}^n \left(\frac{C((\gamma-1)\Delta t) + C(\gamma\Delta t)}{2} \right) \delta_s(n-\gamma+1) \quad \dots (5)$$

Transport of Solute in the Plug Flow Zone

Let us decompose the plug flow zone into 'm' number of cells of equal size. Let the time to fill one cell be Δt . Therefore, $m = \alpha/\Delta t$, where α is the time required to replace the fluid in the plug flow zone. The volume of each cell = $\{u \Delta t A\}$, in which u is the mean flow velocity, and A is the cross-sectional area of flow. According to the principle of plug flow, the fluid in i^{th} cell is replaced by the fluid from the $(i-1)^{th}$ cell. There is no mixing of the influent with the existing fluid. Adsorption takes place in each cell, which follows Eqn. (5). Performing the mass balance of the i^{th} cell for the j^{th} time step, we get,

$$Au\Delta t C(i-1, j) = Au\Delta t C(i, j)(j-\gamma) + W_p u\Delta t \sum_{\gamma=1}^j \left(\frac{C(i, (\gamma-1)\Delta t) + C(i, \gamma\Delta t)}{2} \right) \delta_s(j-\gamma+1) - W_p u\Delta t \sum_{\gamma=1}^{j-1} \left(\frac{C(i, (\gamma-1)\Delta t) + C(i, \gamma\Delta t)}{2} \right) \delta_s(j-\gamma)$$

Splitting the summation upto $(j-1)^{th}$ term and j^{th} term, and solving for $C(i, j)$ one derives,

$$C(i, j) = \frac{C(i, j-1) \delta_s(1) + \sum_{\gamma=1}^{j-1} (C(i, \gamma-1) + C(i, \gamma)) \left\{ \delta_s(j-\gamma+1) - \delta_s(j-\gamma) \right\}}{\left[1 + \frac{W_p}{2A} \delta_s(1) \right]}$$

$C(i, j)$ is solved in succession starting from $i = 1$ and $j = 1$. $C(0, j) = C_R$ for all j including $j = 0$. $C(i, 0) = 0$ for all $i = 1$ to m . Let us designate the output of the m^{th} cell of the plug flow zone as, $C(m, j) = C_p(j)$, which is input to the 1st thoroughly mixed reservoir.

TRANSPORT OF SOLUTE IN THE 1ST THOROUGHLY MIXED RESERVOIR

In the thoroughly mixed reservoir adsorption also takes place at the wetted perimeter of the reservoir. Considering the mass balance between time, $(n-1)\Delta t$ to $n\Delta t$, one gets,

$$A u T_1 \{ C_1(n) - C_1(n-1) \} = A u \Delta t \left[\frac{(C_p(n-1) + C_p(n))}{2} - \frac{(C_1(n-1) + C_1(n))}{2} \right] - W_p u T_1 \left\{ \sum_{\gamma=1}^n \left(\frac{C_1(\gamma-1) + C_1(\gamma)}{2} \right) \delta_s(n-\gamma+1) - \sum_{\gamma=1}^{n-1} \left(\frac{C_1(\gamma-1) + C_1(\gamma)}{2} \right) \delta_s(n-\gamma) \right\}$$

Solving for $C_1(n)$,

$$C_1(n) = \frac{\frac{C_p(n) + C_p(n-1)}{2} - \frac{W_p T_1}{A \Delta t} \left[\sum_{\gamma=1}^{n-1} \left[\frac{C_1(\gamma-1) + C_1(\gamma)}{2} \right] \left\{ \delta_s(n-\gamma+1) - \delta_s(n-\gamma) \right\} + C_1(n-1) \left[-\frac{1}{2} + \frac{T_1}{\Delta t} \left(1 - \frac{W_p \delta_s(l)}{2A} \right) \right] \right]}{\left[\frac{1}{2} + \frac{T_1}{\Delta t} \left(1 + \frac{W_p \delta_s(l)}{2A} \right) \right]}$$

$C_1(n)$ can be solved in succession starting from $n = m + 1$. $C_1(n) = 0$ for $n \leq m$.

TRANSPORT OF SOLUTE IN THE 2ND THOROUGHLY MIXED RESERVOIR

The outflow of the 1st thoroughly mixed reservoir is the input to the 2nd thoroughly mixed reservoir. It is also assumed that adsorption takes place in the wetted perimeter of the reservoir. Let $C_2(n)$ be the concentration of the effluent from the 2nd thoroughly mixed reservoir. Performing the mass balance between time, $(n-1)\Delta t$ to $n\Delta t$, one obtains,

$$C_2(n) = \frac{\frac{C_1(n) + C_1(n-1)}{2} - \frac{W_p T_2}{A \Delta t} \left[\sum_{\gamma=1}^{n-1} \left[\frac{C_2(\gamma-1) + C_2(\gamma)}{2} \right] \left\{ \delta_s(n-\gamma+1) - \delta_s(n-\gamma) \right\} + C_2(n-1) \left[-\frac{1}{2} + \frac{T_2}{\Delta t} \left(1 - \frac{W_p \delta_s(l)}{2A} \right) \right] \right]}{\left[\frac{1}{2} + \frac{T_2}{\Delta t} \left(1 + \frac{W_p \delta_s(l)}{2A} \right) \right]}$$

$C_2(n)$ can be solved in succession starting from $n = m + 1$. $C_2(n) = 0$ for $n \leq m$.

For $C_R = 1$, $C_2(n)$ is the unit step response function of the hybrid unit. The unit pulse response function coefficient $U(n, \Delta t)$ is given by,

$$U(n, \Delta t) = \frac{C_2(n\Delta t) - C_2((n-1)\Delta t)}{\Delta t} \quad \dots (6)$$

For varying input concentration $C_R(\gamma\Delta t)$, the solute concentration at the outlet of the first hybrid unit, $C_{HCIS}(1, n\Delta t)$, is given by,

$$C_{HCIS}(1, n\Delta t) = \sum_{\gamma=1}^n \left\{ \frac{C_R(\gamma\Delta t) + C_R((\gamma-1)\Delta t)}{2} \right\} U(n-\gamma+1, \Delta t)$$

The concentration in j^{th} hybrid unit is given by,

$$C_{HCIS}(j, n\Delta t) = \sum_{\gamma=1}^n \left\{ \frac{C_{HCIS}(j-1, \gamma\Delta t) + C_{HCIS}(j-1, (\gamma-1)\Delta t)}{2} \right\} U(n-\gamma+1, \Delta t)$$

RESULTS AND DISCUSSION

Results of the unit step and unit pulse response functions of the hybrid model are presented for the following sets of parameters: $R_d(\alpha + T_1 + T_2) = 0, 1$ and 2.5 ; $W_p/A = 0.1$ and 0.5 ; $u = 20$ m/min; $\alpha = 1.7$ min; $T_1 = 2.3$ min; $T_2 = 6.0$ min and $\Delta t = 0.05$ min. For $\alpha = 1.7$ min, and $\Delta t = 0.05$ min, the number of cell in the plug flow zone, $m = \alpha/\Delta t = 34$. The variation of mass adsorbed in the first, and in the last cell, i.e., for $i = 1$, and 34 are shown in Figure 2 for $R_d = 0.1/\text{min}$. As expected the adsorption in the plug flow cells varies with time and converges to the inlet boundary concentration. In the last cell adsorption starts after $t > \alpha$.

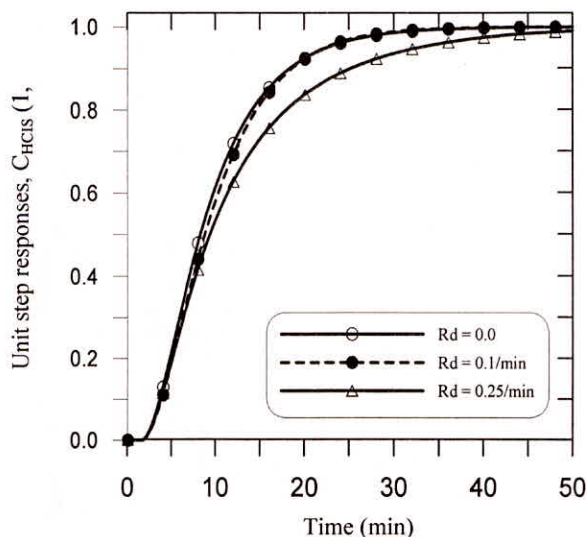


Fig. 2: Absorbed Solute Concentration at the Entry and Exit of the Plug Flow Zone for $R_d (\alpha + T_1 + T_2) = 1.0$, $W_p/A = 0.5$, $U = 20$ m/min, $\alpha = 1.7$ min Corresponding to a Unit Step Input

Mass adsorbed along the plug flow cells at the end of α and $\{10 \alpha\}$ are presented in Figure 3 for values of $W_p/A = 0.1$ and 0.5 for $R_d = 0.1/\text{min}$. From this figure, it could be seen that adsorption varies linearly along the length of the plug flow region. There is no appreciable difference between the concentrations, $C_s(i, j)$ computed for $W_p/A = 0.1$ and 0.5 . As time increases, concentration along the wetted surface converges to the inlet boundary concentration.

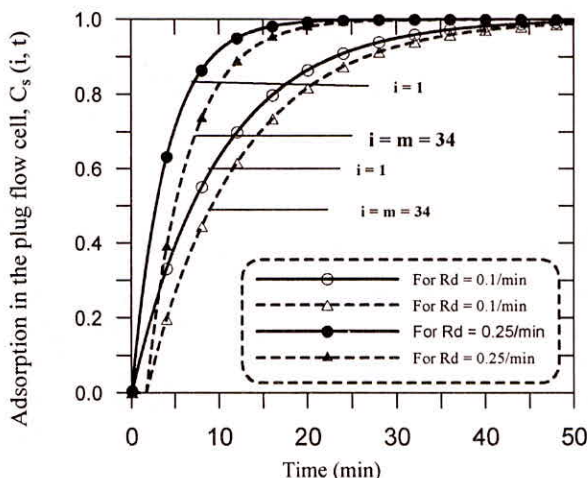


Fig. 3: Variation of Wetted Surface Adsorption in the Plug Flow Cells at the End of a fixed time for $R_d (\alpha + T_1 + T_2) = 1.0$, $U = 20$ m/min, $\alpha = 1.7$ min

The unit step response function of the hybrid unit for values of $R_d = 0.0, 0.1$, and $0.25/\text{min}$ are presented in Figure 4. With higher value of R_d , the concentration

of the effluent converges to the boundary concentration earlier than that for a lower value of R_d . As per Figure 4, in the beginning, for lower value of R_d the solute concentration is close to the graph corresponding to the zero value of R_d . At a particular time in the beginning, the solute concentration corresponding to a higher R_d , is lower than that corresponding to a smaller R_d . This is because; the adsorption is more in the plug flow zone for higher R_d .

At large time, at a particular instant, the solute concentration for higher value of R_d is more than that corresponding to a smaller R_d . This is because, $C_s(i, j)$ converges to boundary concentration more rapidly for higher value of R_d and hence, less adsorption from the incoming solute at large time. That is why the two graphs intersect.

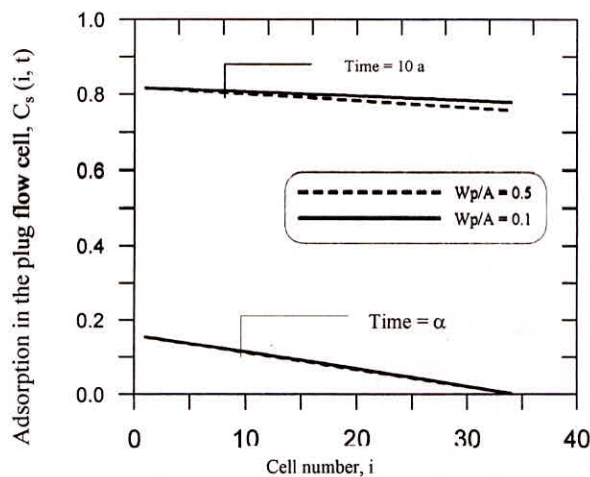


Fig. 4: Response of the Hybrid Unit due to Unit Step Input for $W_p/A = 0.5$, $U = 20$ m/min, $\alpha = 1.7$ min, $T_1 = 2.3$ min, and $T_2 = 6.0$ min

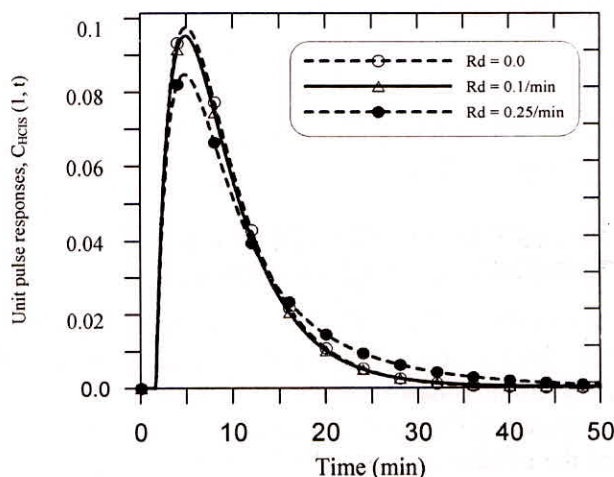


Fig. 5: Response of the Hybrid Unit due to Unit Pulse Input for $W_p/A = 0.5$, $U = 20$ m/min, $\alpha = 1.7$ min, $T_1 = 2.3$ min, and $T_2 = 6.0$ min

The unit pulse response functions of the hybrid model are presented in Figure 5 for values of $R_d = 0.0$, 0.1 and 0.25/min and $\Delta t = 0.05$ min. The unit pulse response function computed using Eqn. (6) for $R_d = 0$ compares well with the response function obtained analytically. Using this unit pulse response function and convolution technique, concentration of the effluent from subsequent stream reaches can be obtained.

CONCLUSIONS

A hybrid-cells-in-series model considering advection-dispersion and adsorption is developed to simulate solute transport in a stream. The non-equilibrium Freundlich type adsorption isotherm has been assumed. Unit step response function and unit pulse response function have been derived. The simplified model can be applied for predicting solute concentrations in natural streams wherein adsorption of solute takes place.

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