

**HWR 516**

**HYDROLOGIC TRANSPORT PROCESSES**

**(Yeh, 1992 Fall)**

**Part 2**

**Lumped Parameter Models for Aquifer Systems**

File: 516-2.wp

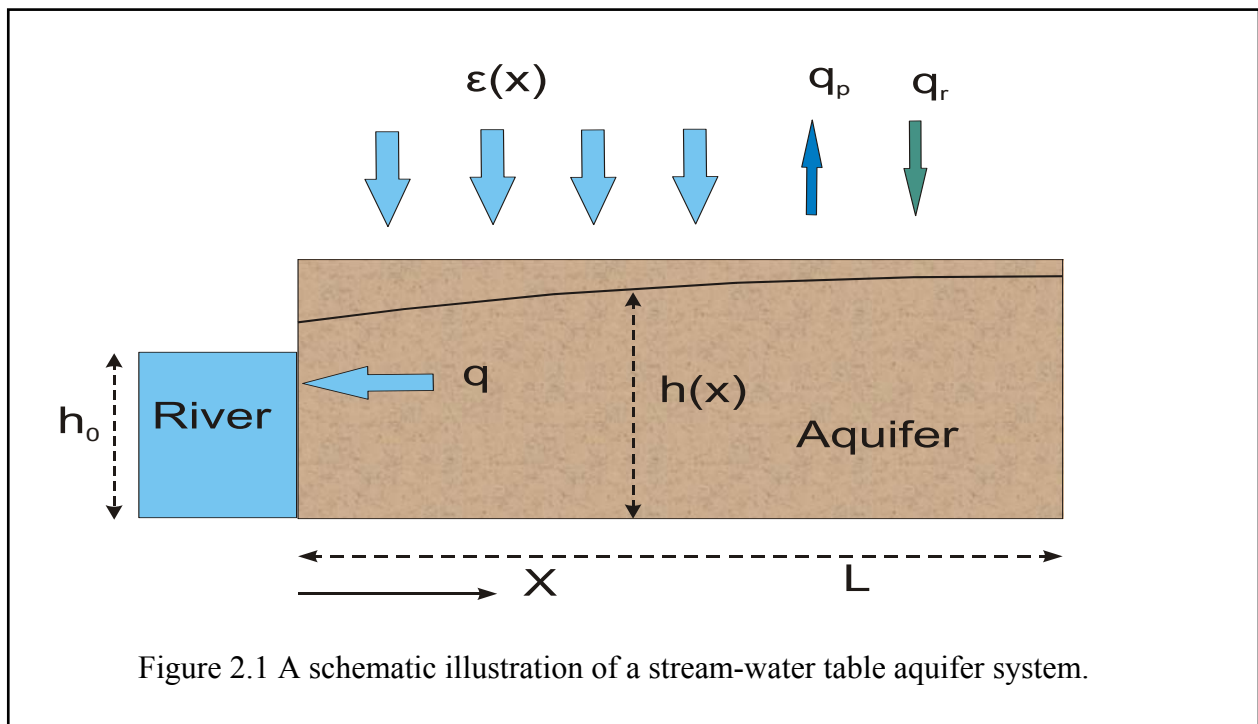
## Chapter 2.

### LUMPED PARAMETER MODELS FOR STREAM-WATER TABLE AQUIFER SYSTEM

See Gelhar & Wilson, *Groundwater*, 12(6), 399-408. Dec. 1974.

#### 2.1 Water Balance Equation

Consider a cross-sectional view of a stream-water table aquifer system as shown in Figure 2.1.



The lower boundary and right-hand side of the aquifer are impermeable. The aquifer is connected to a stream on the left-hand side. The overall water balance for the aquifer can be expressed as

$$\frac{dV}{dt} = R - Q \quad (2.1)$$

where  $V$ ,  $R$ , and  $Q$  are volume, inflow and outflow rates of the aquifer. It also can be written in terms of per unit area:

$$n \frac{d\bar{h}}{dt} = (\bar{\varepsilon} + q_r) - (q - q_p) \quad (2.2)$$

where  $n$  is the average effective porosity (specific yield),  $\bar{h}$  is the average thickness of the saturated zone, i.e.,

$$\bar{h} = \int_0^L h(x) dx / L \quad (2.3),$$

and

$$\bar{\varepsilon} = \int_0^L \varepsilon(x) dx / L \quad (2.4),$$

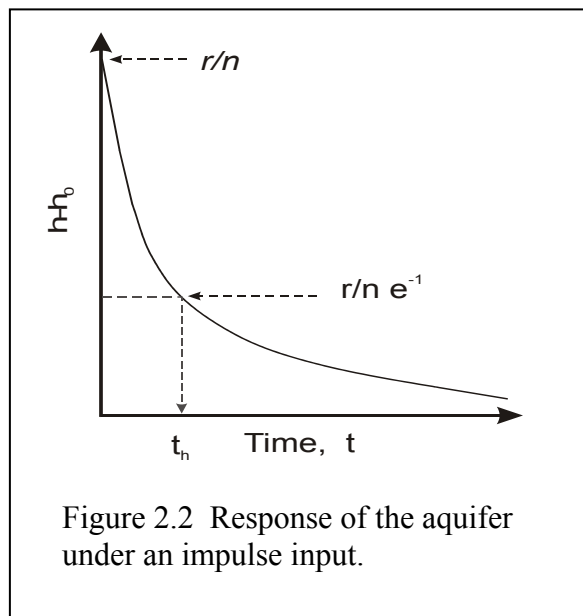
which represents the average recharge rate/area, [L/T].  $q_r$  is the artificial recharge rate/area, [L/T],  $q_p$  is the pumping rate/area, [L/T], and  $q$  denotes the natural outflow rate from the aquifer/area, [L/T]. Next, we will assume inflow and outflow between the aquifer and stream follows a linear reservoir assumption: it is linear proportional to the difference between the average thickness of the saturated zone and the river stage,

$$q = a(\bar{h} - h_o) \quad (2.5)$$

where  $a$  is an outflow constant, [1/T], which is related to aquifer properties and  $h_o$  is the water level in the stream, which can be a function of time. For convenience, we will drop the overhead bar for all the variables. Please bear in mind that all the variables are in the sense of average. If we consider that  $q_r = q_p = 0$ , the water balance equation for the aquifer is

$$n \frac{dh}{dt} + a(h - h_o) = \varepsilon \quad (2.6)$$

which is an ordinary differential equation and it has a closed-form analytical solution, depending on the input type. For an impulse input,



$$\varepsilon = r\delta(t) \quad (2.7)$$

where  $r$  denotes the depth of recharge rate, and  $\delta(t)$  is a Dirac delta function ( $\delta(t)=1$ , when  $t=0$ , and zero otherwise) . The solution associated with this input function is given as

$$h - h_o = \frac{r}{n} e^{-t/t_h} \quad (2.8)$$

where  $t_h = n/a$ , which is called the hydraulic response time [T] of the aquifer. It represents the time required to drain the aquifer to a  $r/n \exp(-1)$  level for a given impulse input of  $\varepsilon$ . It is a characteristic of the aquifer, depending on the values of  $n$  and  $a$ . The behavior of the solution is shown in Figure 2.2.

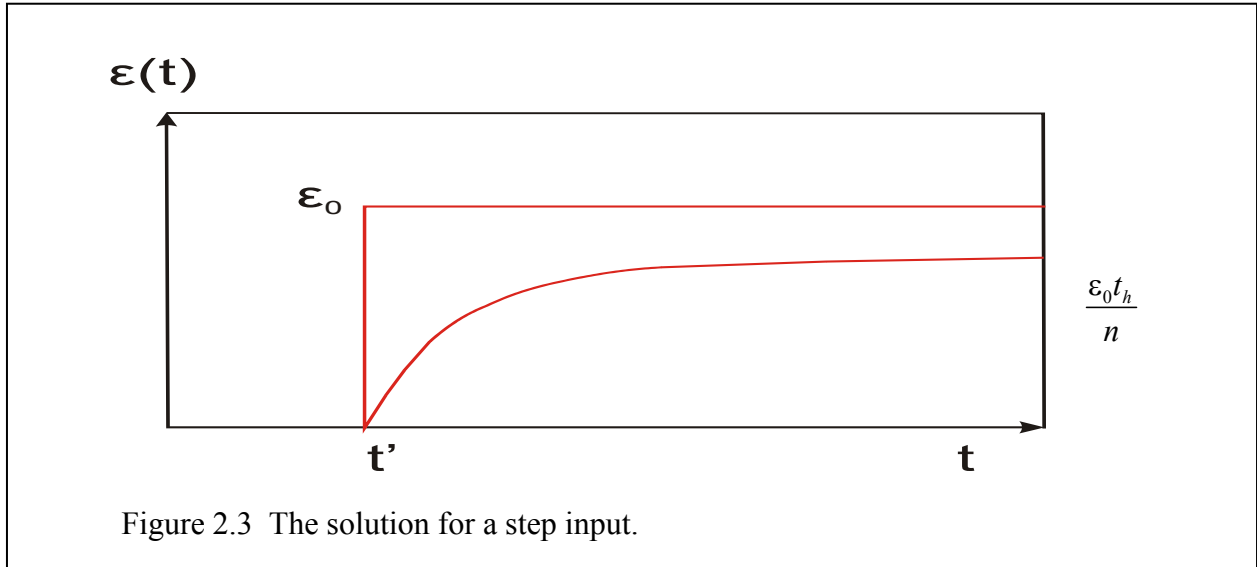
For a step Input of recharge,

$$\varepsilon(t) = \begin{cases} 0 & t < t_1 \\ \varepsilon_o & t \geq t_1 \end{cases} \quad (2.9)$$

The corresponding solution is

$$h - h_o = \frac{\epsilon_o t_h}{n} \left[ 1 - e^{-(t-t_1)/t_h} \right] \quad t > t_1 \quad (2.10)$$

The behavior of the solution is plotted in Figure 2.3.



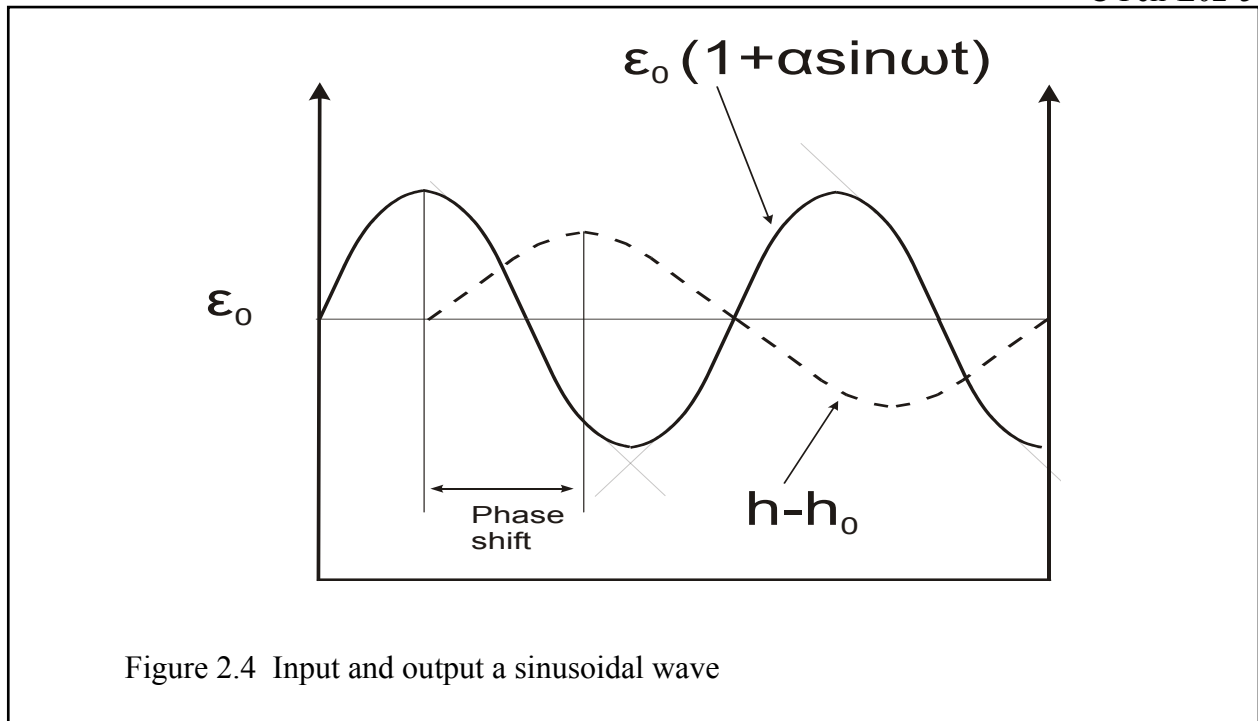
For a sinusoidal input that has the form,

$$\epsilon(t) = \epsilon_o (1 + \alpha \sin \omega t) \quad (2.11)$$

where  $\epsilon_o$  is the base recharge, [L],  $\alpha$  is the amplitude of the sine wave, [L], and  $\omega$  is its frequency, [1/T]. The corresponding solution is given as

$$h - h_o = \frac{\epsilon_o t_h}{n} \left[ 1 + \frac{\alpha}{\sqrt{1 + (t_h \omega)^2}} \right] \sin(\omega t - \phi) \quad (2.12)$$

where  $\phi$  is the phase shift and  $\tan \phi = t_h \omega$



### Parameter Estimation

For field data, cross-correlation analysis of the input and output can be conducted to determine phase shift and attenuation factor. Use phase shift and attenuation factor to estimate,  $a$ , which can be used to determine  $L$ , and  $T$ . Again, one must recognize that the lumped parameter model predicts the average saturated thickness of the aquifer as a function of time. To estimate the parameters of the model, one must use averages of the observed heads. In addition, parameter values obtained represent the parameters for the lumped parameter model only and it represents spatial average values of the parameters.

### 2.1.4 Verification of Linear Reservoir Assumption

Based on the Dupuit assumption, a one-dimensional steady flow for the stream-water table aquifer system can be written as

$$\frac{d}{dx} \left( Kh \frac{dh}{dx} \right) = -\varepsilon \quad (2.13)$$

with boundary conditions:  $x = 0, h = h_o$  and  $x = L, Kh \frac{dh}{dx} = 0$ . The solution can be obtained by integration and is

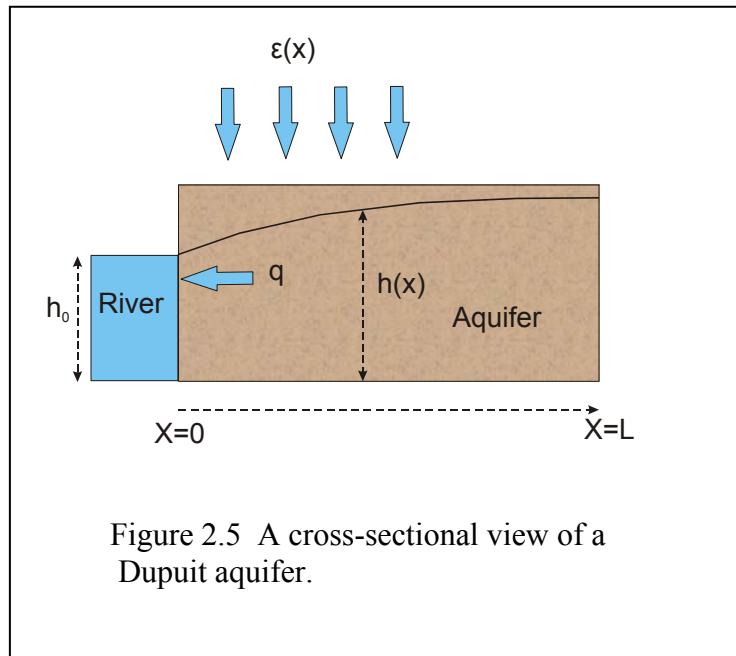


Figure 2.5 A cross-sectional view of a Dupuit aquifer.

$$h^2 - h_o^2 = \varepsilon x(2L - x) / K \quad (2.14)$$

which can be expressed as

$$(h - h_o)(h + h_o) = \varepsilon x(2L - x) / K$$

if  $h - h_o \ll h_o \Rightarrow h \approx h_o$ , we have

an approximate solution:

$$h - h_o = \frac{\varepsilon x(2L - x)}{2T} \quad (2.15)$$

where  $T = Kh_o$ . Subsequently, the average thickness of the saturated zone can be obtained by

$$\bar{h} = \frac{1}{L} \int_0^L \left( \frac{\varepsilon x(2L - x)}{2T} + h_o \right) dx = \frac{\varepsilon L^2}{3T} + h_o$$

(2.16)

Since this is steady flow,  $\varepsilon = q$ .

Recall the linear reservoir assumption used in the lumped parameter model,

$$\varepsilon = q = a(h - h_o) \quad (2.17)$$

Comparing the assumption with the solution, one can derive the constant for the linear reservoir model,

$$a = \frac{3T}{L^2} \left[ \frac{1}{T} \right],$$

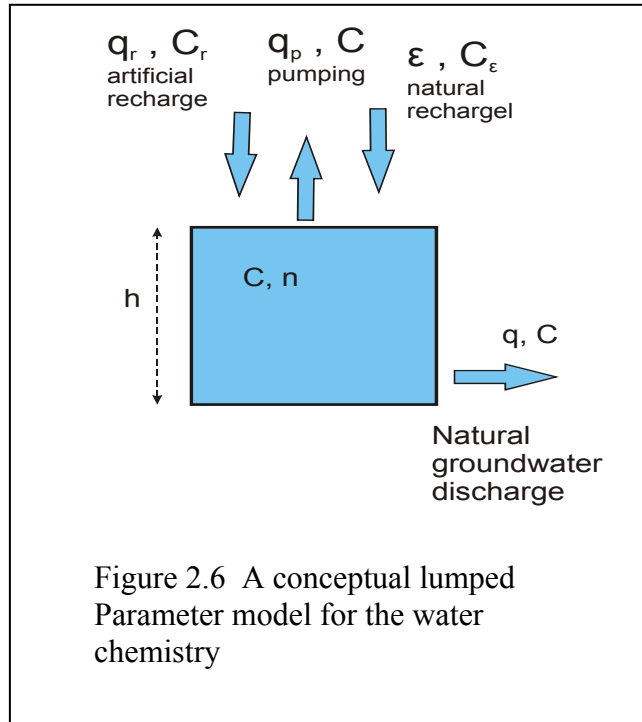
where  $T$  is the transmissivity. This shows that the linear reservoir assumption is valid for aquifers that can be described by the Dupuit assumption.

## 2.2 Water Quality Formulation

We will consider the chemical mass balance for a stream-aquifer system. If we focus on spatially averaged concentration,

$$\bar{C} = \int_0^h \int_0^L C(x, z, t) dx dz / \int_0^L h(x) dx, \quad (2.18)$$

the aquifer system can be treated as a well-mixed system (Figure 2.6). Based on the conceptual model, a lumped parameter model can be formulated.



$$n \frac{d(nhC)}{dt} = \varepsilon C_\varepsilon + q_r C_r - q_p C - qC - knhC \quad (2.19)$$

where the last term of the above equation represent the sink term.

$$nh \frac{dC}{dt} + nC \frac{dh}{dt} = \varepsilon C_\varepsilon + q_r C_r - q_p C - qC - knhC \quad (2.20)$$

Recall the water balance equation,

$$n \frac{dh}{dt} = \varepsilon + q_r - q_p - q \quad (2.21)$$

Therefore, equation (2.20) becomes

$$\frac{dC}{dt} + \frac{(\varepsilon + q_r + knh)}{nh} C = \frac{\varepsilon C_\varepsilon + q_r C_r}{nh} \quad (2.22)$$

The disappearance of  $q_p$  and  $q$  is due to the well-mixed system assumption and their

effects are incorporated in the temporal variation of  $h$ . Now, we let

$$k_e = \frac{\varepsilon + q_r}{nh} + k = k_r + k \quad (2.23)$$

where  $k_r = (\varepsilon + q_r)/nh$ , called the retention constant;  $k$  is the first-order decay constant. The response time of chemicals of the aquifer system is defined as

$$t_c = k_e^{-1} \quad (2.24)$$

It denotes the time at which the chemical concentration will drop to  $e^{-1}$  level due to mixing and chemical reaction in the aquifer.

The chemical mass balance equation can be solved for either steady flow or unsteady flow situations. First, we consider the steady flow condition, in which the saturated thickness of the aquifer does not change with time. Then the water balance equation,

$$n \frac{dh}{dt} + a(h - h_o) = \varepsilon + q_r - q_p \quad (2.25)$$

becomes

$$a(h - h_o) = q = \varepsilon + q_r - q_p \quad (2.26)$$

which states that inflow equals the outflow. From this equation, the steady thickness of the saturated zone can be determined and can be used in the following chemical mass balance equation:

$$\frac{dC}{dt} + \frac{(\varepsilon + q_r + knh)}{nh} C = \frac{\varepsilon C_\varepsilon + q_r C_r}{nh} \quad (2.27)$$

For simplicity, we let  $q_r = 0$  and we have

$$\frac{dC}{dt} + \left( \frac{\varepsilon}{nh} + k \right) C = \frac{\varepsilon}{nh} C_\varepsilon \quad (2.28)$$

For an impulse input of a concentration,  $C_\varepsilon$ , into an aquifer with an initial concentration,  $C_0 = 0$ , the solution is

$$C(t) = C_\varepsilon e^{-k_e t} = C_\varepsilon e^{-t/t_c} \quad (2.29)$$

where  $t_c = k_e^{-1}$ , the chemical response time of the aquifer and  $k_e = (\varepsilon/nh + k)$ .

For a step input, the solution is

$$C(t) = C_\varepsilon \frac{k_r}{k_e} \left( 1 - e^{-t/t_c} \right) \quad (2.30)$$

For a linear increase in input concentration,  $C_\varepsilon = \alpha t$ , where  $\alpha$  is a constant, the solution is given as

$$C(t) = \alpha \left[ (t - t_c) + t_c e^{-t/t_c} \right] \quad (2.31)$$

For large  $t \gg t_c$ , the solution becomes

$$C(t) = \alpha(t - t_c) \quad (2.32)$$

The equation shows that the output concentration lags behind the input concentration by the response time  $t_c$ .

The chemical response under unsteady flow, both the water balance equation and chemical mass balance equation must be solved.

$$n \frac{dh}{dt} + a(h - h_o) = \varepsilon + q_r - q_p \quad (2.33)$$

$$\frac{dC}{dt} + \frac{(\varepsilon + q_r + knh)}{nh} C = \frac{\varepsilon}{nh} C_\varepsilon + \frac{q_r}{nh} C_r \quad (2.34)$$

A more general approach suitable for any arbitrary form of input is a finite difference approach. If we use a finite difference approach to discretize the flow equation in time, we then have

$$n \frac{(h_{i+1} - h_i)}{\Delta t} + a \left( \frac{h_{i+1} + h_i}{2} - h_o \right) = \varepsilon_i + q_{ri} - q_{pi} \quad (2.35)$$

where subscript  $i$  is the time step index and the solution is given by

$$\left( 1 + \frac{1}{2} \frac{\Delta t}{t_h} \right) h_{i+1} = h_i - \frac{\Delta t}{2t_h} h_i + \frac{\Delta t}{t_h} h_o + \Delta t \frac{(\varepsilon_i - q_{ri} - q_{pi})}{n} \quad (2.36)$$

where  $t_h = n/a$  is the hydraulic response time. Similarly, we can discretize the chemical mass balance equation to obtain

$$C_{i+1} - C_i = -\frac{\Delta t}{n} \left[ (\varepsilon_i + q_i) \left( \frac{C_{i+1} + C_i}{2} \right) - (\varepsilon_i C_{\varepsilon i} + q_{ri} C_{ri}) \right] \left( \frac{2}{h_{i+1} + h_i} \right) \quad (2.37)$$

Once the h's at different time are obtained, they can be used in this equation to calculate the concentration at various time.

### Hydraulic response time, retention time, and chemical response time.

Hydraulic response time,  $t_h$ , is the time required for the ground water system to dissipate a sudden increase of  $h$  due a recharge of  $\varepsilon$  ( $\Delta h = \varepsilon/n$ ) to a  $\Delta h e^{-1}$  level as shown in Figure 2.2. It is related to the aquifer characteristics,  $t_h = n/a$ . On the other hand, the chemical response time is defined as the time required for the system to dissipate a sudden increase of concentration,  $C_\varepsilon$ , to  $C_\varepsilon e^{-1}$  level. The chemical response time is the reciprocal of  $K_e$ ,

$$t_c = \frac{1}{k_e} \quad (2.38)$$

where

$$k_e = \frac{\varepsilon}{nh} + k \quad (2.39)$$

if conservative chemicals are considered,  $k = 0$ ,

$$t_c = \frac{1}{k_r}, \quad (2.40)$$

where  $k_r$  is the reservoir retention time, which is defined as the amount time required to fill the entire aquifer with the given recharge,  $\varepsilon$ . That is,

$$t_r = \frac{nh}{\varepsilon} \quad (2.41)$$

Generally speaking, the chemical response time,  $t_c$ , is greater than the hydraulic response time,  $t_h$ , (see Table 1, Gelhar and Wilson, 1974.)

### Application of the Model

#### 1. Highway Salt on Groundwater Quality (Eastern Massachusetts)

Water balance model

$$n \frac{dh}{dt} + a(h - h_o) = \varepsilon \quad (2.41)$$

Chemical mass balance model,

$$nh \frac{dC}{dt} + \varepsilon C = \varepsilon C_\varepsilon \quad (2.42)$$

we will assume that  $q_r = q_p = 0$ , and  $C_r = 0$  since groundwater withdrawn is approximately 2 inch/yr and recharge through septic tank is minimal. Solutions for the two equations were obtained by using finite difference analogs of (2.41) and (2.42) with  $\Delta t = 1$  month. Required input parameters,  $\varepsilon$ ,  $C_\varepsilon$ ,  $n$ , and  $a$ , are estimated as follows:

Estimation of Input parameters:

1. Recharge rate,  $\varepsilon$ , (inches/month). In order to determine the monthly recharge rate, it is assumed that the annual recharge,  $\bar{\varepsilon}$ , is linearly proportional to the annual precipitation,  $\bar{P}$ .

$$\bar{\varepsilon} = 0.35 \bar{P}$$

Then, the annual recharge is distributed over January through May according to the figure below.

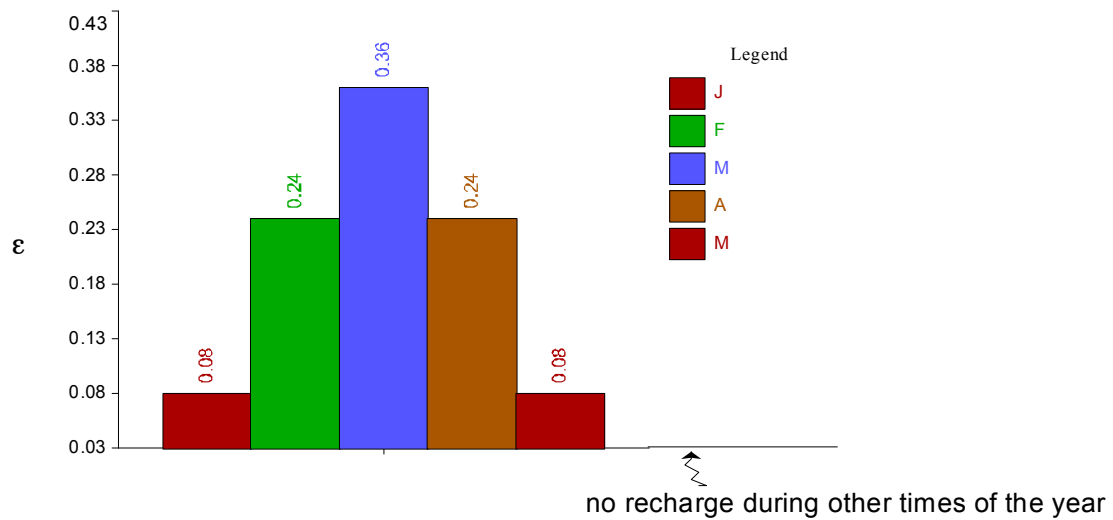


Figure 2.7

## 2. Salt Input:

Based on city government's record, 12 tons / lane mile /year road salt had been used, and the width of highway is assumed to be 15ft. This leads to an estimate of the amount of road salt used per square highway area.

$$\frac{12 \times 2000 lb}{15 ft \times 5280 ft} = \frac{0.3 lb Salt}{ft^2 Highway}$$

If highway density is 5 % of the aquifer area, the road salt per aquifer area becomes

$$\frac{0.3 lb Salt}{ft^2 Highway} \times \frac{5 (\text{area of highway})}{100 (\text{area of Aquifer})} = 1.5 \times 10^{-2} \frac{lb Salt}{ft^2 Aquifer}$$

One could multiply this with the fraction of salt that actually reaches the water table. If annual precipitation is

$$\begin{aligned} \bar{P} &= 4 ft/yr & \bar{\varepsilon} &= 0.35 \times 4 = 1.4 ft/yr \\ C_{\varepsilon} &= \frac{\text{Mass of Salt}}{\text{Mass of Water}} = \frac{1.5 \times 10^{-2} lb/ft^2}{1.4 f \times 62.4 lb/ft^3} = 1.72 \times 10^{-4} = 172 \underbrace{\times 10^{-6}}_{ppm} \\ &= 172 ppm \end{aligned}$$

## 3. Aquifer Parameters

Assume:

$$n = 0.25$$

$$h_o = 25, \underline{50}, 100 \text{ ft}$$

$$t_h = \frac{n}{a} = 6 \text{ months}$$

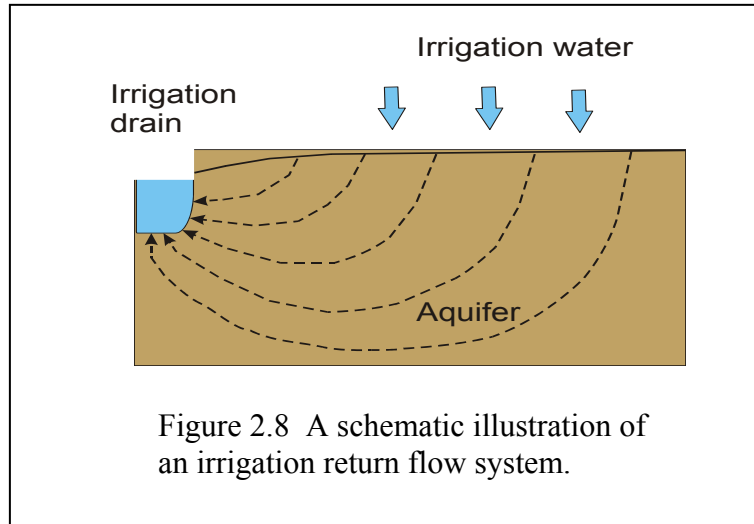
Determine  $h(t)$ . (See Fig. 3)

$$\begin{aligned} t_c &= \text{chemical response time} \\ &= \frac{n h}{\varepsilon} = \frac{0.25 \times 50 ft}{1.4 ft/yr} = 8.9 \text{ yrs.} \end{aligned}$$

Slow change in water quality.

## 2. Irrigation Return Flow

Irrigation drainage systems have been installed at many farms in many regions, where groundwater table is shallow, for collecting irrigation water to maintain desired water table height at the farms. This drain discharge is called the irrigation return flow (see Figure 2.?).

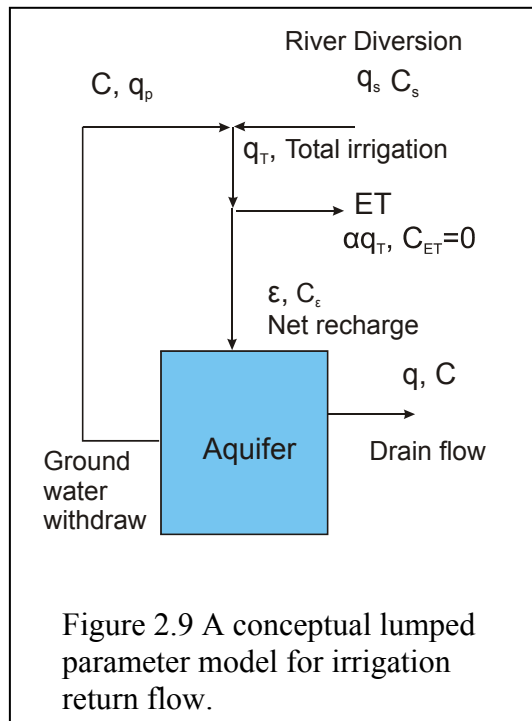


The irrigation return flow in general is high in chemicals associated with fertilizers. It has been observed that farming along upstream of a river can have significant impact of water quality at downstream. Major sources modifying the river water quality have been found to be the irrigation return flow, which discharges back into the river. In this section we will formulate lumped parameter models for estimating water quality of the

irrigation return flow.

Before the formulation of the mathematical model, it is desirable to build a conceptual model. The conceptual model treats the aquifer as a well-mixed box and specifies all input and output processes involved as illustrated in the figure below.

Major sources of irrigation water are water diverted from rivers during wet seasons and groundwater withdrawal from aquifers during dry seasons. That is,



Total applied irrigation water = river diversion + ground water withdrawal from aquifer,

$$q_T = q_s + \beta q_T$$

in which  $q_T$  is the total irrigation water,  $q_s$  is the river diversion, and  $\beta$  is the fraction of the total irrigation water that is coming from ground water withdrawal. If we assume the system is under steady flow, then the net recharge to the aquifer is

$$\varepsilon = (1 - \alpha)q_T = q + \beta q_T$$

where  $\alpha$  is the fraction of the total applied irrigation water is returned to atmosphere by evapotranspiration. The discharge to the drain becomes

$$q = (1 - \alpha - \beta)q_T$$

and the concentration associated with the net recharge can be determined by

$$C_{\varepsilon} = \frac{q_s C_s + \beta q_T C}{(1 - \alpha) q_T}$$

Accordingly, the chemical mass balance equation becomes

$$nh \frac{dC}{dt} = \varepsilon C_{\varepsilon} - qC - \beta q_T C \quad \text{or} \quad nh \frac{dC}{dt} = q_s C_s - qC$$

Assuming that the concentration of the chemical in the river diversion,  $C_s$  is time invariant, and that at  $t = 0$ ,  $C(t) = C_o$ , then the solution to the chemical mass balance equation is

$$C(t) = C_o e^{-k_r t} + \frac{q_s}{q} C_s (1 - e^{-k_r t})$$

When time approaches infinite, the steady concentration becomes

$$C(\infty) = \frac{q_s C_s}{q} = \frac{(1 - \beta) q_T}{(1 - \alpha - \beta) q_T} C_s = \frac{(1 - \beta)}{(1 - \alpha - \beta)} C_s$$

According to this result, evapotranspiration essentially increases the concentration of total dissolved solutes in the irrigation return flow even though no chemicals from fertilizers have been considered in this case.

Next, we will consider unsteady flow problem:

$$n \frac{dh}{dt} = \varepsilon - q - \beta q_T = (1 - \alpha) q_T - a(h - h_o) - \beta q_T$$

Since we know that

$$q_T (1 - \beta) = q_s$$

we then have the water mass balance equation:

$$n \frac{dh}{dt} + a(h - h_o) = \frac{(1 - \alpha - \beta)}{(1 - \beta)} q_s$$

If the input form of  $q_s$  is given, the saturated thickness of the aquifer at any time can be determined, and then it can be used in the chemical mass balance equation. In general, it is easier to solve the two equations using numerical methods.

### Unsaturated – Saturated Systems

Of course, a lumped parameter can be formulated for the vadose zone. Consider the water balance and if we integrate a one-dimensional Richards equation over the vertical and assume that upward or downward flow is proportional to the head difference between the vadose zone and its lower system (i.e., aquifers), we then have

$$C(h) \frac{\partial h}{\partial t} = \frac{\partial \theta}{\partial t} = q - a[(h - h_0) + 1]$$

where  $h$  is the average pressure head,  $\theta$  is the average moisture content,  $q$  is the flux on the land surface,  $a$  is a parameter which is a function of  $K(h)$ , unsaturated hydraulic conductivity,  $h_0$  is the pressure at the water table, which is zero, and the last term is the gravity term. The equation can be further simplified if we assume the vadose zone is under unit-gradient condition and the unsaturated hydraulic conductivity function follows an exponential function, we then have

$$\frac{\partial \theta}{\partial t} = q - K(\theta) = q - K_s \exp(\beta\theta)$$

The equation is nonlinear and numerical approach may be necessary. The calculated  $\theta$  can be used to evaluate the hydraulic conductivity function, which is the outflow to the aquifer below. Therefore, the model can be linked with the previously established stream-aquifer system.

**Multilayered Aquifers:** Similarly, the lumped parameter approach can be applied to a multilayered aquifer. Each layer can be treated as a lumped parameter model and all aquifers can be linked as a series. As the number of lumped systems increases, the series or parallel (or a mixture of series and parallel systems) system approaches a finite difference approximation of the partial differential equation that describes groundwater flow through porous media.

## MODEL CALIBRATION FOR THE MESILLA VALLEY (D. Updegraf, M.S. study, 1977)

### Data available:

Monthly water levels in 39± wells over several years

Monthly drain flow (acre-feet/month)

Monthly irrigation diversion (ac-ft/mo)

### Lumped Parameter Model

$$S \frac{dh}{dt} + a(h - h_0) = r_{ij} + u_i$$

where  $h$  is the water level average over a month, [ L ],  $S$  is the average storage coefficient (i.e., effective porosity, [ ]),  $a$  is the linear reservoir constant, [1/T],  $h_0$  is the linear outflow datum,  $r_{ij}$  is the variable recharge averaged over a month, and  $u_i$  is the leakage (constant during a given year,  $i$ ). Our objective here is to estimate parameters of the model,  $S$ ,  $a$ ,  $h_0$ ,  $r_{ij}$  and  $u_i$ , where  $i$  and  $j$  are the year and month index, respectively.

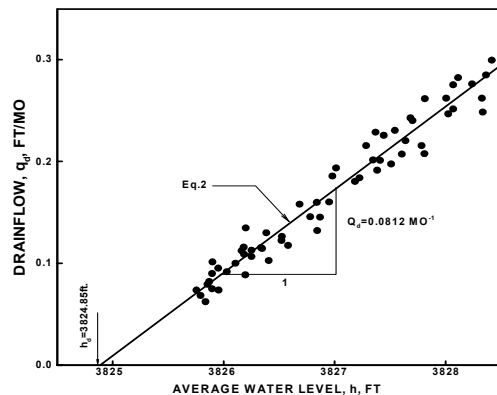


Figure 2.10 Regression analysis of drain flow and average water level data in Mesilla Valley, New Mexico.

### Parameter Estimation procedure

The estimation procedure involves the following steps.

1) Apply linear regression to estimate the parameters,  $a$ , and  $h_0$ , using drain flow and water level data, and the linear reservoir model,  $q = a(h - h_0)$ , by minimizing

$$\sum_{ij} (\hat{q}_{ij} - q_{ij})^2 = \text{minimal}$$

where  $\hat{q}_{ij}$  is the observed water level averaged over the basin and  $q$  is the simulated one using the lumped model.

2) Find  $S$  and  $u$  from recessions when  $r = 0$ . First integrate the equation over the month

$$\int_{j+}^{j+1} S \frac{dh}{dt} dt + a \int_{j-1}^{j+1} (h - h_0) dt = \int_{j-1}^{j+1} u dt$$

Then use a finite difference approach for approximating the equation and we have

$$S \left( \frac{h_{j+1} - h_{j+}}{2\Delta t} \right) 2\Delta t + a \int_{j-1}^{j+1} h dt - a \int_{j-1}^{j+1} h_0 dt = \int_{j-1}^{j+1} u dt$$

where  $\Delta t = t_j - t_{j-1}$ . After rearranging the equation, we obtain

$$S \left( \frac{h_{j+1} - h_{j-1}}{2\Delta t} \right) 2\Delta t + a \left( \frac{h_{j-1} + 4h_j + h_{j+1}}{3} - ah_o \right) 2\Delta t = u_j 2\Delta t$$

and

$$S(h_{j+1} - h_{j-1}) + a \left[ \frac{(h_{j-1} + h_j + h_{j+1})}{3 \cdot 2} - h_o \right] 2\Delta t = u 2\Delta t$$

If we let

$$x = (h_{j+1} - h_j) \text{ and}$$

$$y = a \left[ \frac{(h_{j-1} + h_j + h_{j+1})}{3 \cdot 2} - h_o \right] 2\Delta t$$

we have a linear equation

$$y = \alpha x + \beta_i$$

where  $\alpha = -S$  and  $\beta_i = 2u_i \Delta t$ . Since  $x$  and  $y$  are known from data and previous parameter estimation, a linear regression determines the values of  $\alpha$  and  $\beta_i$ .

3) Find recharge  $r$  from integrated equation with  $r \neq 0$

$$S(h_{j+1} - h_{j-1}) + a \int_{j-1}^{j+1} (h - h_o) dt - 2u\Delta t = \frac{\Delta t}{3} (r_{j-1} + 4r_j + r_{j+1})$$

The left-hand side of the equation is known because of the previous estimates of the parameters,  $S$ ,  $a$ , and  $u$ , and the data of  $h$  at different times. The right-hand side contains the unknowns, which represents the recharge at different months. As a result, we have a system of linear equations for  $r_j$  at different months, which forms a tri-diagonal matrix.

4) Results:  $S = 0.21$ ,  $a = 0.0812$  / month ( $T_h = 2.59$  month)

Recharge pattern figure 7C.

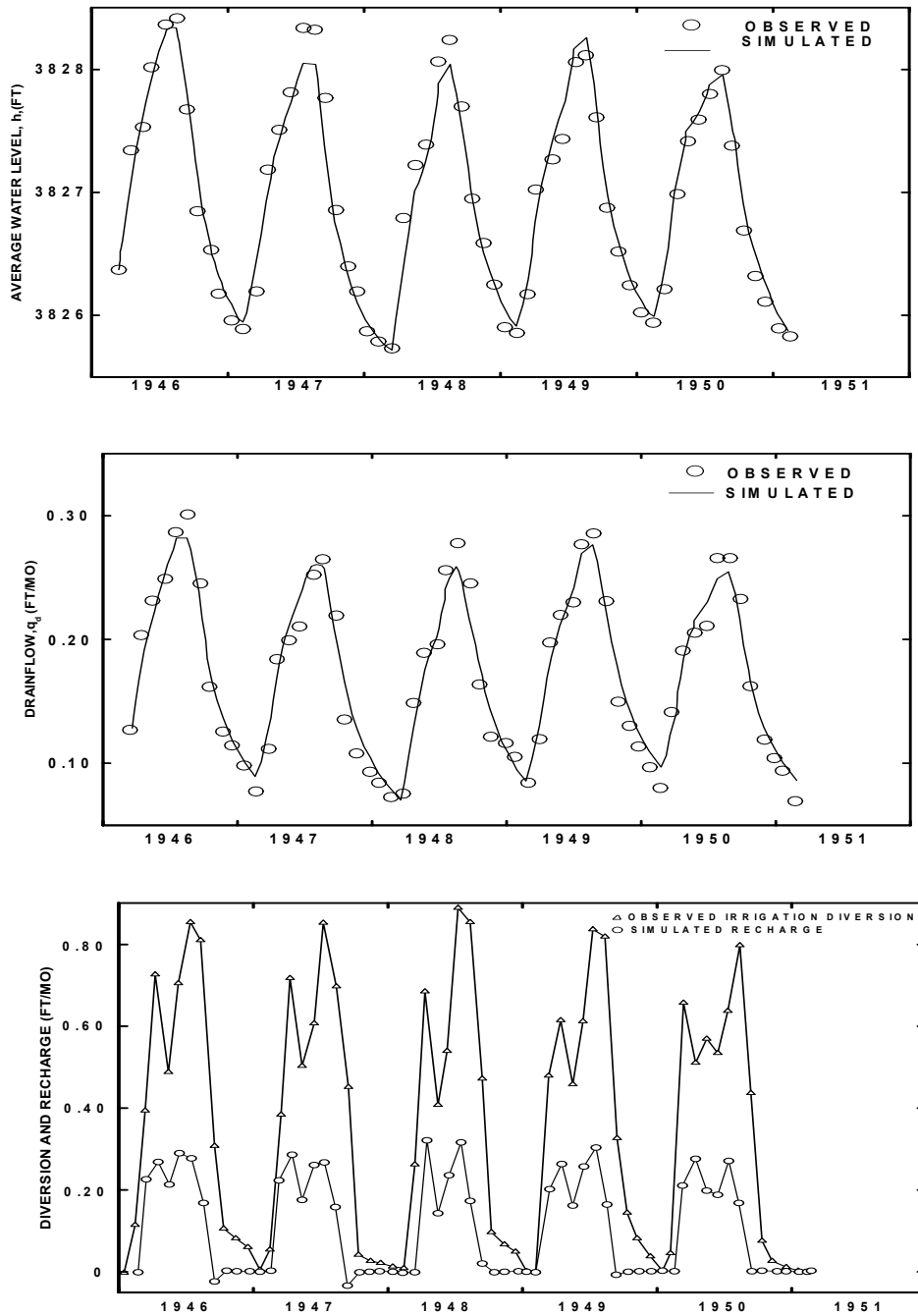


Figure 2.11 a) Simulated and observed water level, b) simulated and observed drain flow, c) observed river diversion and estimated groundwater recharge.

## Lumped Parameter Models for reactive Chemicals

Unsteady Flow

1. Water balance:

$$n \frac{dh}{dt} = \varepsilon - q$$

2. Chemical mass balance of water phase:

$$n \frac{dhC}{dt} = C \varepsilon - Cq - S \quad \text{if } q_p = q_r = 0$$

$\rho = \text{constant}$

$S = \text{sink or source term}$

Chemical reactions, representing ion exchange (adsorption and desorption)

Consider a unit volume of porous media.

Vol. fraction of solid =  $1 - n$

If we define the density of solid as

$$\rho_s = \frac{M_s}{V_s}$$

and the bulk density of the porous medium is

$$\rho_b = \frac{M_s}{V_T}$$

The relationship between the bulk density and solid density is

$$\rho_s = \frac{M_s/V_s}{V_T/V_s} = \frac{\rho_b}{1/(1-n)} = (1-n)\rho_b$$

Now, let  $C_s$  be the concentration of chemical  $\alpha$  in the solid, which is the ratio of mass of  $\alpha$  to the mass of solid, [ppm].

### Mass Balance for Solid Phase:

Change of mass in solid phase *per*  $V_T =$  net mass of  $\alpha$  removed from or added to the fluid *per*  $V_T$

For a unit volume of a porous medium, the mass balance equation for the solid phase is

$$\frac{d\rho_s(1-n)C_s}{dt} = n\rho\gamma$$

where  $\gamma$  is the reaction rate constant, [1/T]. The equation can also be written in terms of the bulk density as

$$\frac{d\rho_b C_s}{dt} = n\rho\gamma$$

Dimension analysis of the equation yields

$$\left[ \frac{M_s}{V_T} \right] \left[ \frac{M_\alpha}{M_s} \right] \left[ \frac{1}{T} \right] = \left[ \frac{V_w}{V_T} \right] \left[ \frac{M_w}{V_w} \right] \left[ \frac{M_\alpha}{TM_w} \right]$$

or

$$\frac{\rho_b}{n\rho} \frac{dC_s}{dt} = \gamma$$

Now, we need to relate the concentration in the solid phase to the concentration in the liquid phase. Two types of chemical reaction models are considered.

**(1) Equilibrium Model.** This model assumes that the chemical reaction time between the solid and liquid phase is instantaneous or in other words, the chemical reaction time is much smaller than groundwater residence time (the time for groundwater traveling through a unit volume of a porous medium). The common equilibrium model used is the linear isotherm model:

$$C_s = aC \quad \left[ \frac{M_\alpha}{M_s} \right] = \left[ \frac{M_w}{M_s} \right] \left[ \frac{M_\alpha}{M_w} \right]$$

which assumes that the concentration in the solid phase is linearly proportional to the concentration in the liquid phase. In the equation  $a$  is a dimensionless partition coefficient,  $C$  and  $C_s$  are the concentration of  $\alpha$  in fluid and solid phase, respectively. This equation leads to

$$\frac{dC_s}{dt} = a \frac{dC}{dt}$$

Therefore, the mass balance equation can be rewritten in terms of the concentration in the liquid phase:

$$\gamma = \frac{\rho_b}{n\rho} a \frac{dC}{dt} = \frac{\rho_b}{n} K_d \frac{dC}{dt}$$

where  $K_d$  is the distribution coefficient, i.e.,

$$K_d = \frac{a}{\rho} \left[ \frac{M_w}{M_s} \right] \left[ \frac{V_w}{M_w} \right] = \left[ \frac{L^3}{M} \right]$$

Using the result of the above analysis for the sink or source term,  $S = nh\gamma$  in the mass balance equation for  $\alpha$ , we have

$$\frac{dC}{dt} + \frac{\varepsilon}{nh}C = \frac{\varepsilon}{nh}C_\varepsilon - \frac{\rho_b}{n}K_d \frac{dC}{dt}$$

Rearrange the equation yields

$$\left(1 + \frac{\rho_b}{n}K_d\right) \frac{dC}{dt} + \frac{\varepsilon}{nh}C = \frac{\varepsilon}{nh}C_\varepsilon$$

If we define the retardation factor as

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

which is a dimensionless parameter, then we have

$$\frac{dC}{dt} + \frac{\varepsilon}{nhR}C = \frac{\varepsilon}{nhR}C_\varepsilon$$

If we further define a chemical retention constant,

$$k_{cr} = \frac{\varepsilon}{nhR},$$

it's reciprocal is the chemical retention time,  $t_{cr}$ ,

$$t_{cr} = \frac{nhR}{\varepsilon}$$

The effect of the chemical reaction,  $R > 1$ , is to increase the chemical retention time. If  $R = 1$ , a conservative chemical, its chemical retention time is the same as the groundwater retention time. For chemicals that can undergo both decay, adsorption, and desorption, the mass balance equation is

$$\frac{dC}{dt} + (k_{cr} + k)C = k_{cr}C_\varepsilon$$

The overall effect of chemical reaction between solid and liquid phase and the chemical decay is increasing the chemical response time.

**(2) Non-Equilibrium Model.** This model considers chemicals that do not react with solids instantaneously, or its chemical equilibrium time is much larger than the groundwater retention time. In this case, the mass balance for the solid phase, assuming a first-order reaction, is given

$$\frac{dC_s}{dt} = \beta(C - C_e)$$

where  $\beta$  is the first-order reaction rate,  $[1/T]$ , and  $C_e$  denotes the equilibrium concentration in liquid phase. That is,

$$C_e = \frac{C_s}{a} \quad \text{or} \quad C_s = aC_e$$

Subsequently, the mass balance equation for the chemical in the liquid phase is

$$\frac{dC}{dt} + \frac{\varepsilon}{nh}C = \frac{\varepsilon}{nh}C_\varepsilon - \frac{\rho_b\beta}{n\rho} \left( C - \frac{C_s}{a} \right)$$

To determine the chemical concentration in either solid or liquid phase, the mass balance equations for the solid and liquid phases have to be coupled and solved simultaneously.

$$\begin{cases} \frac{dC}{dt} + \left( k_r + \frac{\rho_b}{\rho n} \beta \right) C = k_r C_e + \frac{\rho_b}{\rho n} \beta \frac{C_s}{a} \\ \frac{dC_s}{dt} + \frac{\beta}{a} C_s = \beta C \end{cases}$$

Use Laplace Transform to solve the system of equations.

The non-equilibrium model (1<sup>st</sup> Order) is basically a linear model that has a time varying reaction rate. Consider the model,

$$\frac{dC_s}{dt} = \beta(C - C_e)$$

where  $C_e = C_s/a$ . Using this relationship, the mass balance equation can be rewritten as

$$\frac{dC_s}{dt} + \frac{\beta}{a} C_s = \beta C$$

For a given chemical concentration in the liquid phase, the concentration in the solid phase is

$$C_s(t) = aC \left( 1 - e^{-\frac{\beta}{a}t} \right)$$

if  $C_s(0) = 0$ . Based on this equation, at  $t$  approaches infinite, the model essentially becomes an equilibrium model:

$$C_s(\infty) = aC$$

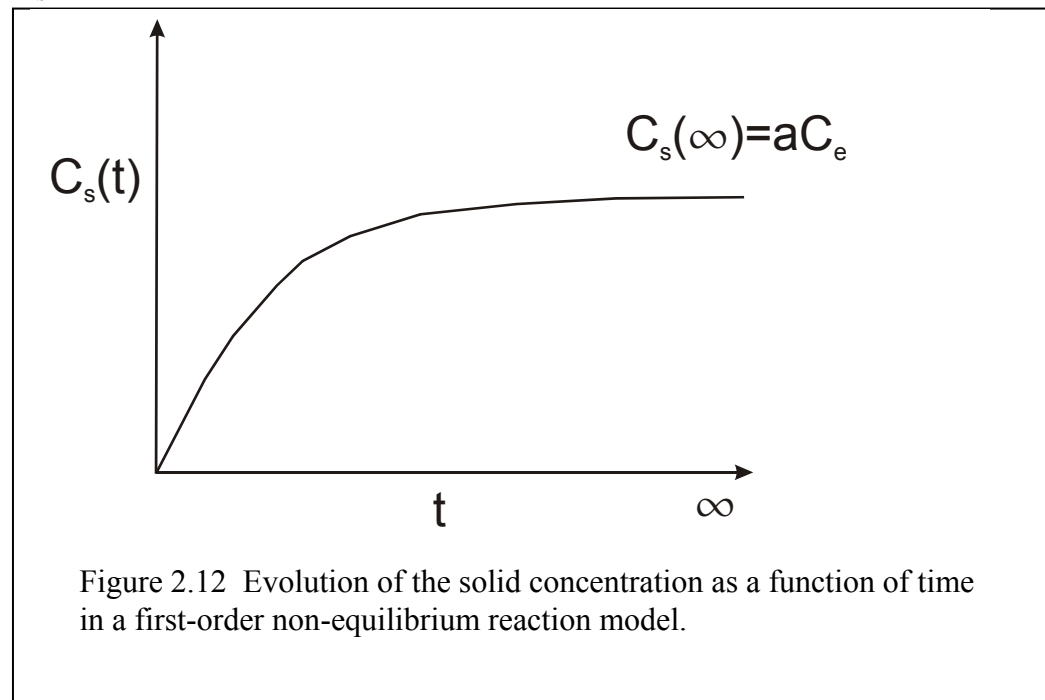


Figure 2.12 Evolution of the solid concentration as a function of time in a first-order non-equilibrium reaction model.

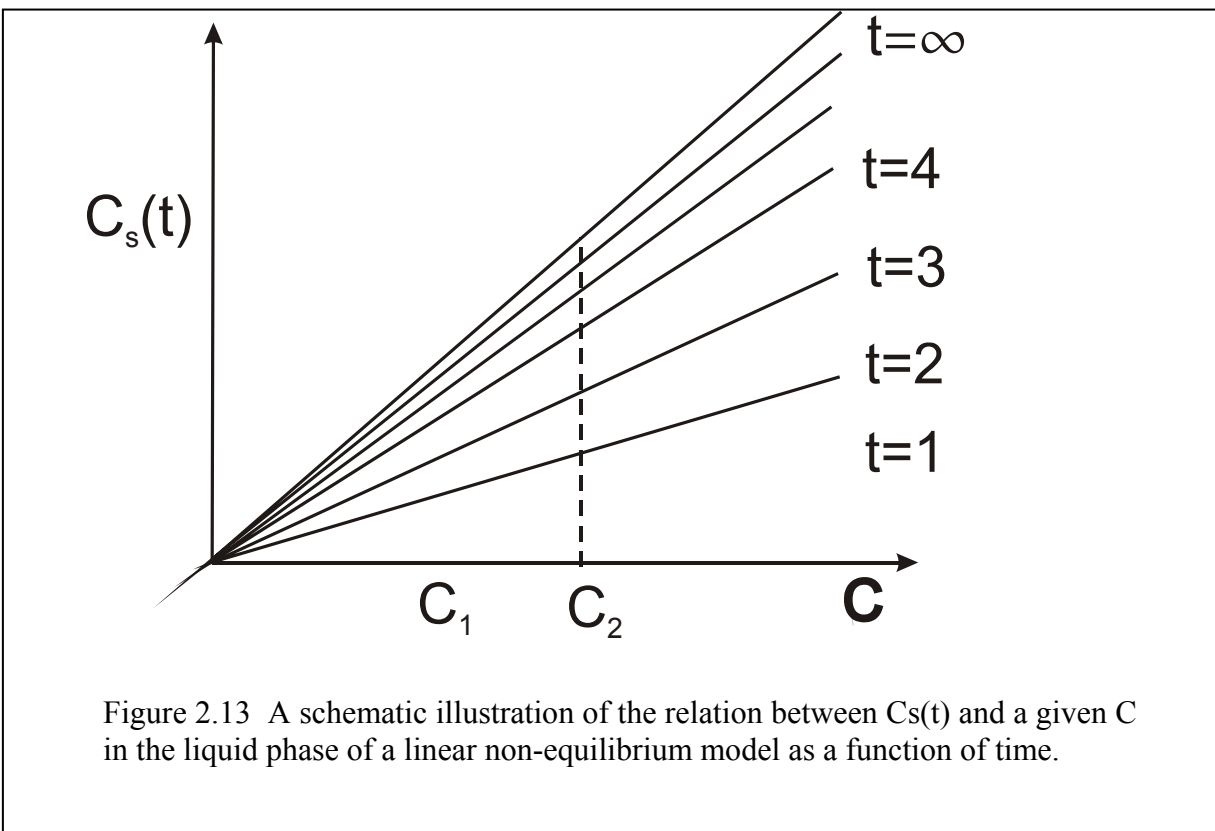
If we reexamine the problem in a different way, for a given  $t = t^*$ , the solid concentration is related to any liquid concentration,  $C$ , by

$$C_s(t^*) = a \left( 1 - e^{-\frac{\beta}{a} t^*} \right) C$$

which can be rewritten as

$$C_s(t^*) = A(t^*)C$$

In this case, the reaction constant,  $A$ , is a time-dependent variable. However, at any given time, the model for the reaction between the solid and liquid phase is merely a linear one as illustrated in Figure 2.10.



Two Site Model:

$$\frac{dC}{dt} + \frac{\rho_b}{n\rho} \frac{dC_{S1}}{dt} + \frac{\rho_b}{n\rho} \frac{dC_{S2}}{dt} + k_r C = k_r C_\varepsilon$$

The first site assumes an equilibrium model

$$C_{S1} = a_1 C$$

which leads to

$$\frac{dC_{S1}}{dt} = a_1 \frac{dC}{dt}$$

The second site assumes a non-equilibrium model,

$$\frac{dC_{S2}}{dt} = \beta \left( C - \frac{C_{S2}}{a} \right)$$

After combining these equations, the equation for the mass balance of the chemical in both liquid phase and solid phase are:

$$\left( 1 + \frac{\rho_b a}{\rho n} \right) \frac{dC}{dt} + \frac{\rho_b}{n\rho} \frac{dC_{S2}}{dt} + k_r C = k_r C_\varepsilon$$

$$\frac{dC_{S2}}{dt} = \beta \left( C - \frac{C_{S2}}{a} \right)$$

These two equations have to be solved simultaneously.

Non-Equilibrium Lumped Parameter Model

$$\begin{cases} \frac{d \bar{n} \bar{h} C}{dt} = \varepsilon C_1 + q_r C_r - q_p C - q C - \bar{n} \bar{h} \frac{\rho_b}{\bar{n} \rho} k_r \left( C - \frac{C_s}{a} \right) \\ \frac{d C_s}{dt} = k_r \left( C - \frac{C_s}{a} \right) \end{cases}$$

$\varepsilon$  : net recharge  
 $q_r$  : recharge rate  
 $q_p$  : pumping rate  
 $q$  : outflow rate  
 $\rho_b$  : bulk density  
 $\rho$  : pore fluid density  
 $k_r$  : reaction constant  
 $a$  : retardation factor

Where  $\rho_b =$  the bulk density  $\rho_s(1 - n)$   
 $k_r =$  reaction constant

Rearrange terms; the system of O.D.E. becomes

$$\begin{cases} \frac{dC}{dt} + \left( \frac{R}{nh} + \frac{\rho_b}{\rho n} k_r \right) C = \frac{RC_R}{nh} + \frac{\rho_b}{\rho n} k_r \frac{C_s}{a} \\ \frac{dC_s}{dt} + \frac{k_r}{a} C_s = k_r C \end{cases}$$

where  $R = \varepsilon + q_r \rightarrow$  net recharge, and we assume  $C_1 = C_r$

Let  $k_e = \frac{R}{nh} + \frac{\rho_b}{\rho n} k_r$

$$\begin{cases} \frac{dC}{dt} + k_e C = \frac{RC_R}{nh} + \frac{\rho_b}{\rho n} k_r \frac{C_s}{a} \\ \frac{dC_s}{dt} + \frac{k_r}{a} C_s = k_r C \end{cases}$$

Let  $C(0) = C_o$  when  $t = 0$

$$C_s(0) = C_{s0}$$

Use Laplace Transform,

$$\begin{aligned} \mathcal{L}(f') &= S \mathcal{L}(f) - f(0), & \text{let } \mathcal{L}(C) &= Y \\ \mathcal{L}(C_s) &= Y_s \end{aligned}$$

$$\begin{cases} SY - C(0) + k_e Y = \frac{RC_R}{nh} \left( \frac{1}{S} \right) + \frac{\rho_b k_r}{n\rho a} Y_s \\ SY_s - C_s(0) + \frac{k_r}{a} Y_s = k_r Y \end{cases}$$

$$\begin{cases} (S + k_e)Y - \left( \frac{\rho_b k_r}{n\rho a} \right) Y_s = \left( \frac{RC_R}{nh} \right) \frac{1}{S} + C_o \\ -k_r Y + \left( S + \frac{k_r}{a} \right) Y_s = C_{s_o} \end{cases}$$

Solve these simultaneous equations.

$$Y = \frac{\frac{1}{S} \left( \frac{RC_R}{anh} \right) + C_o S + C_o \left( \frac{RC_R}{nh} \right) + \frac{\rho_b}{n\rho} \left( \frac{RC_R}{nh} \right) C_{s_o}}{\left[ S^2 + \left( k_e + \frac{k_r}{a} \right) S + \frac{k_e k_r}{a} - \frac{a\rho_b}{n\rho} \left( \frac{k_r^2}{a^2} \right) \right]}$$

$$\text{Let } A = \frac{RC_R}{nh} \quad B = \frac{\rho_b}{n\rho} \quad D = k_e + \frac{k_r}{a}$$

$$E = \left( \frac{k_e k_r}{a} - \frac{a\rho_b}{n\rho} \left( \frac{k_r^2}{a^2} \right) \right)$$

$$\therefore Y = \frac{\left( \frac{A}{a} \right) \frac{1}{S} + C_o (S + A) + BAC_s}{(S^2 + DS + E)}$$

$$x = \frac{-D + \sqrt{D^2 - 4E}}{2}$$

$$y = \frac{-D - \sqrt{D^2 - 4E}}{2}$$

$$Y = \frac{A}{a} \frac{1}{S(S+x)(S+y)} + \frac{C_o(S+A)}{(S+x)(S+y)} + \frac{BAC_s}{(S+x)(S+y)}$$

$$C = \frac{A}{a} \left( \frac{1}{xy} - \frac{ye^{-xt}}{xy(x-y)} - \frac{xe^{-yt}}{xy(x-y)} \right) + C_o \left( \frac{ye^{-yt} - xe^{-xt}}{y-x} + \frac{A(e^{-xt} - e^{-yt})}{y-x} \right)$$

$$BAC_s \left( \frac{e^{-xt} - e^{-yt}}{y-x} \right)$$

## Sensitivity and Uncertainty Analysis (First-Order Approximation)

Using the Taylor Series expansion, a nonlinear function can be written as

$$f(x + \Delta x) = f(x) + \overbrace{\Delta x f'(x)}^{\text{first order}} + \underbrace{\frac{\Delta x^2}{2} f''(x) + \dots}_{\text{higher order}}$$

A first-order approximation retains the zero<sup>th</sup> and second-order terms of the Taylor series expansion such that

$$f(x + \Delta x) - f(x) \approx \Delta x f'(x)$$

If we say that  $x$  is the mean of a parameter of a function and  $\sigma_x$  is the perturbation (uncertainty) of the parameter, we can use the 1<sup>st</sup> order analysis to determine the uncertainty of a output associated with the uncertain input. If  $y$  is the output of a system with an input with uncertainty,

$$y = f(x)$$

the mean of the output is assumed to be

$$E[y] \approx f(\mu_x)$$

This assumption is strictly valid if  $f$  is a linear function. If we express the input as mean plus the perturbation:

$$x = \mu_x + x'$$

where  $\mu_x = E[x]$  and  $E$  denotes the expectation. According to the first-order approximation of the output, we have

$$y(x) \approx E(y) + \left. \frac{df}{dx} \right|_{\mu_x} (x - \mu_x)$$

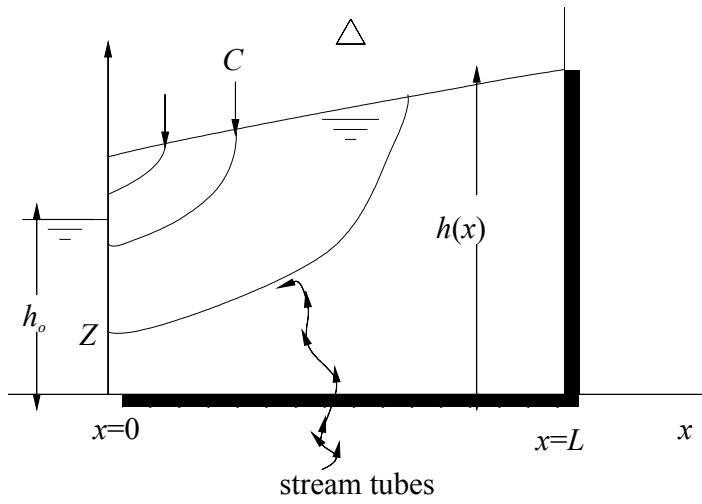
in which the derivative of  $f$  is evaluated at the mean value of the parameter and it is called the sensitivity of the output to the change in the parameter value. Then, the variance of the output is given as

$$E\left\{[y - E[y]]^2\right\} = \left. \frac{df}{dx} \right|_{\mu_x}^2 E\left[(x - \mu_x)^2\right]$$

and can be simplified to

$$\sigma^2 y = \left( \left. \frac{df}{dx} \right|_{\mu_x} \right)^2 \sigma^2 x$$

Based on this first-order analysis, one needs to find the derivative of the function, evaluate it at the mean parameter value, and use the equation to obtain the variance in output.



→

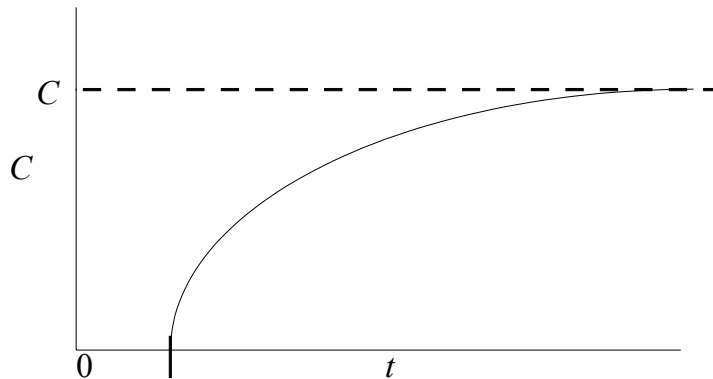
Verification of the Well-Mixed Assumption for Stream-Aquifer Systems.

If  $C_{\text{ini}}$  is released simultaneously over the water table, which contaminant particle will arrive at the stream?

The one close to the stream.

The one far away from the stream will arrive later.

Based on this logic, the “average concentration” at  $x = 0$  as a function of time, if a step input is applied should be:



This behavior is similar to the solution obtained from the well-mixed, lumped parameter model.

A rigorous

analysis requires steady flow to be solved.

$$\frac{\partial}{\partial x} \left( K \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial z} \left( K \frac{\partial h}{\partial z} \right) = \varepsilon$$

and free-surface boundary conditions

$$\frac{K}{n_e} \left[ \left( \frac{\partial h}{\partial x} \right)^2 + \left( \frac{\partial h}{\partial z} \right)^2 - \frac{\partial h}{\partial z} \left( 1 + \frac{\varepsilon}{K} \right) + \frac{\varepsilon}{K} \right] = 0$$

and

$$q_x = -K \frac{\partial h}{\partial x} = 0 \quad \text{at} \quad x = L$$

$$h = h_o \quad \text{at} \quad x = 0$$

and at seepage face  $h = z$

If we neglect dispersion 滲 no mixing between tubes 滲 piston type displacement

Use FREESURF

head distribution

stream lines

stream tubes

Displace each slug of contaminant, then average the concentration at  $x = 0$ . This concentration is the outflow concentration from the aquifer.

Alternative:

To approximate the streamline:

Approximate shape of the water table.

$$h - h_o = \frac{\varepsilon}{2T} x(2L - x) \quad (1)$$

where  $T = K h_o$

This equation is derived based on the Dupuit Assumptions, i.e., horizontal flow.

We will assume this is the W.T. shape that has vertical flow.

Horizontal Component (Specific Discharge)

$$\begin{aligned} q_x &= -K \frac{\partial h}{\partial x} = -K \frac{\partial(h - h_o)}{\partial x} \\ &= \frac{\varepsilon(L - x)}{h_o} \end{aligned}$$

Vertical Component

$$q_z = -K \frac{\partial h}{\partial z}$$

We cannot use this approach because eq. (1) is z-independent.

From Continuity Eq. (Steady Flow)

$$q_z = -\int_0^z \frac{\partial q_x}{\partial x} dz = -\int_0^z \frac{\varepsilon}{h_o} dz = -\frac{\varepsilon z}{h_o}$$

Coordinate of any particles on the front.

$$\text{Vertical velocity } \frac{dz^*}{dt} = \frac{q_z}{n} \Big|_{z=z^*} = -\frac{\varepsilon z^*}{nh_0}$$

Solution:

$$z^* = Ae^{-\varepsilon t/nh_0}$$

when  $t = 0$ , i.e., when the contaminant is introduced

$$h(x) = A$$

$$\therefore z^*(x, t) = h(x)e^{-\varepsilon t/nh_0}$$

vertical position at  $t$  of the particle released at  $x$ , or  $h(x)$

X - coordinate

$$\frac{dx^*}{dt} = \frac{q_x}{n} \Big|_{x=x^*} = -\frac{\varepsilon(L-x^*)}{nh_0}$$

Solution

$$(L-x^*) = Ae^{\varepsilon t/nh_0}$$

$$\text{at } t=0, \quad x^* = x_0 \quad \Rightarrow \quad A = L - x_0$$

$$\therefore (L-x^*) = (L-x_0)e^{\varepsilon t/nh_0}$$

$$x^* = L + (x_0 - L)e^{\varepsilon t/nh_0}$$

The time required for a contaminant particle to leave the aquifer:

$$\text{i.e., } x^* = 0 \quad L = (L-x_0)e^{\varepsilon t/nh_0}$$

$$\text{or } t = \frac{nh_0}{\varepsilon} \ln \left( \frac{L}{L-x_0} \right)$$

Recall

$$z^*(x, t) = h(x) e^{-t/t_c} \quad \text{where } t_c = \frac{n h_o}{\varepsilon}$$

and

$$h(x) - h_o = \frac{\varepsilon}{2T} x(2L - x) = \frac{\varepsilon}{2T} [L^2 - (L - x)^2]$$

and  $(L - x_o) = (L - x^*) e^{-t/t_c}$

$$\begin{aligned} z^*(x_o, t) &= \left\{ \frac{\varepsilon}{2T} [L^2 - (L - x_o)^2] + h_o \right\} e^{-t/t_c} \\ &= \left\{ \frac{\varepsilon}{2T} [L^2 - (L - x^*)^2 e^{-2t/t_c}] + h_o \right\} e^{-t/t_c} \end{aligned}$$

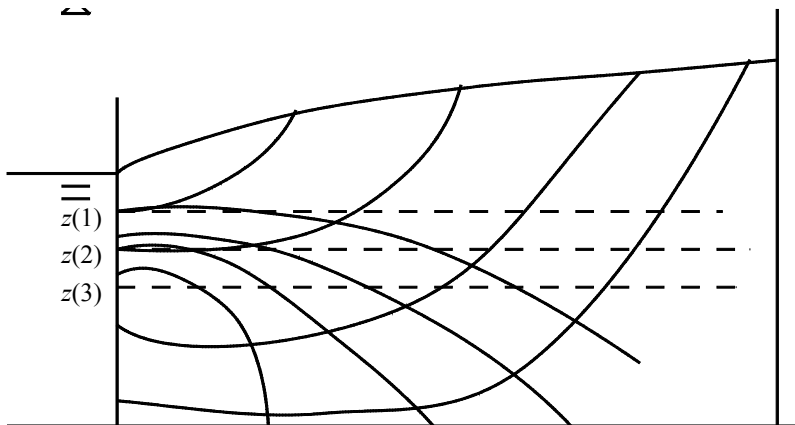
now let  $x^* = 0$

$$z^*(t) = \left\{ \frac{\varepsilon}{2T} [L^2 - L^2 e^{-2t/t_c}] + h_o \right\} e^{-t/t_c}$$

or

$$z^*(t) = \left\{ \frac{\varepsilon L^2}{2T h_o} [1 - e^{-2t/t_c}] + 1 \right\} h_o e^{-t/t_c}$$

This is the vertical position of the front at  $x = 0$ . Exit vertical position.



Simplification

Let  $x = L$  to check the magnitude of  $\frac{\varepsilon L^2}{2T h_o}$

$$\Delta h = h(x) - h_o = \frac{\varepsilon L^2}{2T}$$

$$\frac{\Delta h}{h_o} = \frac{\varepsilon L^2}{2T h_o}$$

$$\text{if } h_o \gg \Delta h \quad \Rightarrow \quad \frac{\varepsilon L^2}{2T h_o} \ll 1$$

Now recall

$$z^*(x, t) = h(x) e^{-t/t_c} \quad \text{where} \quad t_c = \frac{n h_o}{\varepsilon} \quad (\text{a})$$

and

$$h(x) - h_o = \frac{\varepsilon x}{2T} (2L - x) = \frac{\varepsilon}{2T} [L^2 - (L - x)^2] \quad (\text{b})$$

and

$$(L - x_o) = (L - x^*) e^{-t/t_c} \quad (\text{c})$$

Therefore, the vertical position of a particle that originated at  $x_o$  is:

$$\begin{aligned} z^*(x_o, t) &= \left\{ \underbrace{\frac{\varepsilon}{2T} [L^2 - (L - x_o)^2] + h_o}_{h(x)} \right\} e^{-t/t_c} \\ &= \left\{ \frac{\varepsilon}{2T} \left[ L^2 - \underbrace{(L - x^*)^2}_{\text{from (c)}} \right] e^{-2t/t_c} + h_o \right\} e^{-t/t_c} \end{aligned}$$

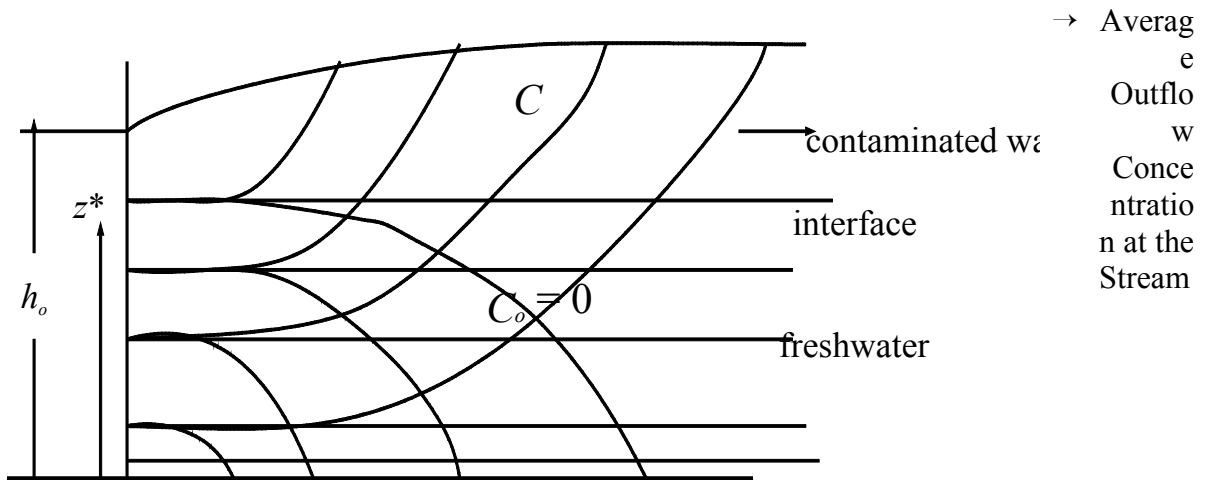
Now let  $x^* = 0$  at the stream-aquifer interface:

$$z^*(t) = \left\{ \frac{\varepsilon L^2}{2T} (1 - e^{-2t/t_c}) + h_o \right\} e^{-t/t_c}$$

This is the vertical position of the front at  $x = 0$  at any  $t$ .

This implies that:

$$z^*(t) \approx h_o e^{-t/t_c}$$



$$h_o C = (h_o - \bar{z}^*) C_\varepsilon + \bar{z}^* C_o$$

where  $C$  = average concentration in outflow

$$C = C_\varepsilon \left( 1 - \frac{\bar{z}^*}{h_o} \right)$$

$$C(t) \approx C_{\varepsilon} (1 - e^{-t/t_c})$$

similar to the solution of M.B. equation for a step input.

→ Average Concentration in the Aquifer

$$C h(x) = (h(x) - z^*(x, t)) C_\varepsilon$$

$$C = \frac{1}{L} \int_0^L \frac{C_\varepsilon (h(x) - z^*(x, t))}{h(x)} dx$$

$$= \frac{1}{L} \int_0^L C_\varepsilon \left( 1 - \frac{z^*(x, t)}{h(x)} \right) dx$$

$$C(t) = C_\varepsilon (1 - e^{-t/t_c})$$

Dimensionless Analysis of one-dimensional transport equation for reactive solutes.

$$\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} = D_L \frac{\partial^2 C}{\partial x^2} - (1-f) \frac{\partial C_1}{\partial t}$$

$$(1-f) \frac{\partial C_1}{\partial t} = \gamma(C_1 - C)$$

$$\text{Let } \eta = \frac{x}{L}, \quad \tau = \frac{ut}{L}$$

$$\frac{\partial C}{\partial \tau} + \frac{\partial C}{\partial \eta} = \left( \frac{D}{uL} \right) \frac{\partial^2 C}{\partial \eta^2} - (1-f) \frac{\partial C_1}{\partial \tau}$$

$$(1-f) \frac{\partial C_1}{\partial \tau} = \frac{L\gamma}{u} (C_1 - C)$$

or

$$\frac{\partial C}{\partial \tau} + \frac{\partial C}{\partial \eta} = \left( \frac{D}{uL} \right) \frac{\partial^2 C}{\partial \eta^2} - \left( \frac{L\gamma}{u} \right) (C_1 - C) = \left( \frac{\alpha u}{uL} \right) \frac{\partial^2 C}{\partial \eta^2} - \left( \frac{L}{u} \gamma \right) (C_1 - C)$$

$$\text{If we let } u^* = L\gamma = \left[ \frac{L}{T} \right]$$

we then have

$$\frac{\partial C}{\partial \tau} + \frac{\partial C}{\partial \eta} = \left( \frac{\alpha}{L} \right) \frac{\partial^2 C}{\partial \eta^2} - \left( \frac{u^*}{u} \right) (C_1 - C)$$

For a given concentration, C, in the liquid phase, the concentration in the solid phase is

$$C_1 = C e^{-\frac{L\gamma}{u(1-f)} \tau}$$