

Module: Couple flow and transport

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1. Introduction

This module will introduce groundwater flow with the inclusion of mass. In the study of hydrogeology or groundwater, mass transport or simply transport (also used in this module) is a standard term that describes flow of mass along with groundwater. As it may have already become clear, with a transport we deal with quality aspect of groundwater, as compared to flow in which quantity is dealt. The transport question becomes very important when groundwater is used as a source of potable water, which is required to be maintained at a standard quality but more importantly which is to be protected against the quality deterioration or contamination. Thus with transport we deal with not only the physical aspect of hydrogeology, both subsurface physical properties (e.g., homogeneity versus heterogeneity) and flow dynamics as it is with a flow problem, but we also interlink these with chemical and biological aspects of hydrogeology. Thus, longer terms such as hydrogeochemistry and hydrobiogeochemistry are very frequently encountered in the literature dealing with the groundwater transport problems. The mathematical complexity of the transport problem increases when we have to deal with transient cases, i.e., when the mass of interest is changing with respect to time. A fairly representative transport problem will often require that we set-up at least a $2D$ system. This further adds to the complexity of the problem even when a steady-state case, i.e. mass of interest remains constant with respect to time, can be assumed. As it is with mathematical problems, the difficulty and cost of experimental works, laboratory or field, is dependent on the complexity of problems and the required level of result details. Thus, mathematical modelling is often the first choice, followed by laboratory and field experimentation, in attempting to understand and solve the transport problems.

The transport problem is inherently a multi-disciplinary one, and thus it is important that we first identify different processes (physical, chemical and biological) that are important in describing the problem. We will begin with a non-reacting system, also called a conservative system, which is purely a physical transport problem. Subsequently we will identify reactive processes (chemical and biochemical) and couple them with the physical transport problem, which is then termed as a reactive transport problem. Our approach will remain mostly mathematical as such we will attempt to solve and visualize few examples of transport problems. In this module we will focus on saturated (all voids filled), homogeneous (aquifer properties such as conductivity do not change along the extend) and isotropic (aquifer properties is uniform also in all directions) aquifers.

2. Learning Outcome

This module will present an introductory topics relevant to transport problems in groundwater. Emphasis will be on describing processes, coupling them and eventually establishing the mathematical formulation of the problem. The target groups are higher level undergraduate students and the first year PG students. The module, as it is introductory, will only briefly introduce methods for solving transport problems. The specific objectives of the module are:

- I. Systematic introduction to transport problems in groundwater
- II. Recognizing factors and processes affecting transport problems
- III. Realization why coupling of processes is required to address transport problems
- IV. Developing a systematic approach to solve transport problems.

3. Conservative Transport Processes

Aquifers as we know already are extensive, at least in the horizontal and lateral directions, whereas its properties such as conductivity, transmissivity often changes in a very small scale, in many cases also at a pore-scale. As such to understand aquifer properties and underlying processes, we define a Representative Control Volume (RCV, see Fig 1). Ideally a RCV is very much smaller than the aquifer that is investigated, and at the same it is very much larger than individual grain or pore. The essential condition is that Darcy's law has to be applicable in the RCV. A big advantage of RCV is that in the aquifer processes analysis it can be oriented as per the coordinate system, e.g., rectangular for Cartesian coordinate.

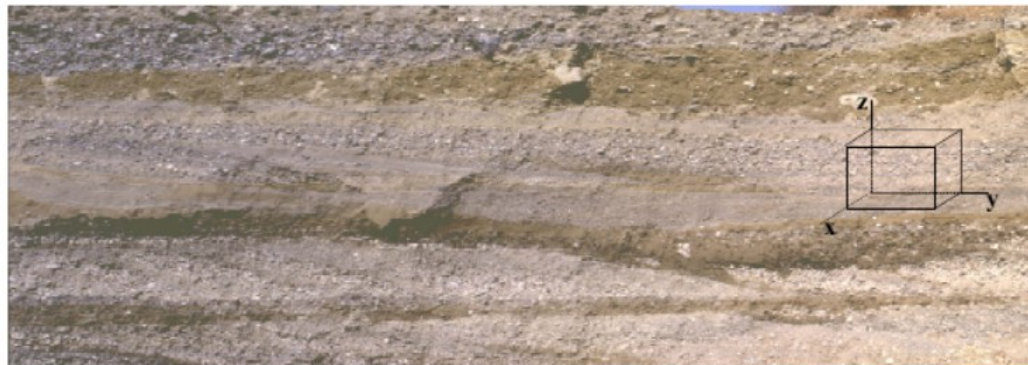


Fig. 1: A schematic RCV imposed on the outcrop.

Now that we have defined our model aquifer volume, a RCV, we will attempt to understand the transport processes. However before we do that let us very briefly differentiate between the conservative and reactive transport (which we will discuss in the next section). A conservative transport is one in which:

1. the mass in question do not interact with the aquifer solid matrix.
2. the mass in question do not interact with other mass dissolved in groundwater.
3. the mass in question do not undergo any mediated changes, e.g., microbial interaction.

In essence, the mass in question remains quantitatively (amount) and qualitatively (chemical properties) unchanged. When any one of the above points are not met we have a reactive transport system. Conservative systems are generally used for quantifying physical transport processes, which are utilized in analysing the reactive systems.

Before we step forward to learn the transport processes, let us perform a couple of simple laboratory column experiments. This should help us understand more clearly the transport processes. Let us assume that we have a column (say diameter = 3 cm, and length = 10 cm) packed homogeneously with aquifer material, e.g., coarse sand. Let us continuously introduce a tracer, say NaCl (concentration C_0), from the entry end of the column instantly at time, t_0 . For tracking the movement of the tracer, we will periodically collect effluent from the column and analyse for NaCl concentration. The results of our hypothetical experiments are presented in Fig. 2. We observe that mass particles in the column was transported in two different ways. In the first case (Fig. 2b) the effluent and inlet concentrations are always equal for all times except the initial lag time, when there are no NaCl leaving the column. Clearly, the mass particles are uniformly pressed out of the column in this case. The particles obtained in effluent are called advected mass, and the transport process is termed advection. The other case (Fig. 2c), suggests that mass particles are travelling with different speeds.

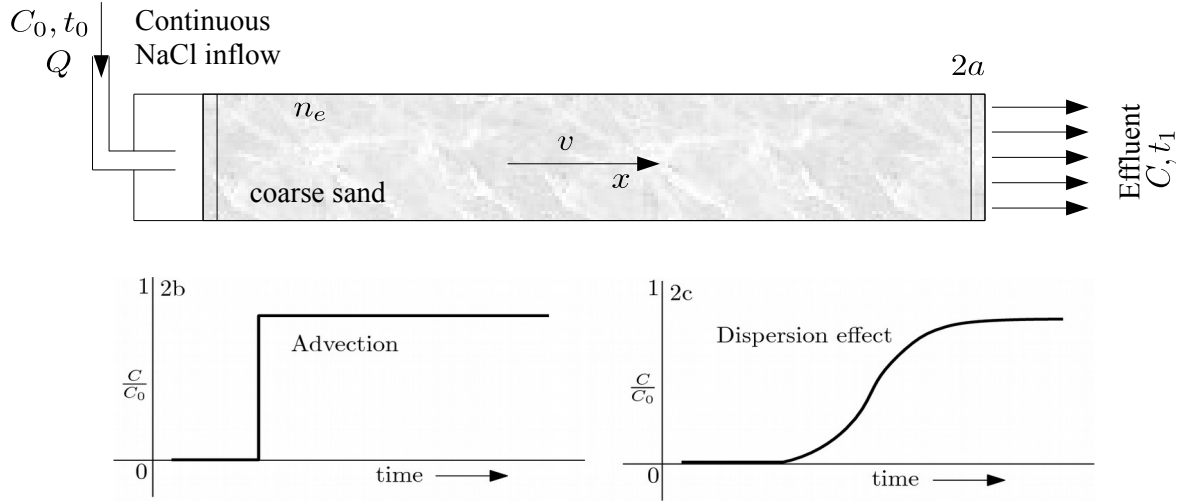


Fig 2: A schematic of a lab column experiment (2a). Fig 2b is the plug-flow type case and Fig 2c presents the case when there is spread of mass during the transport (adapted from Freeze and Cherry, 1979)

In this case the mass particles get spread and therefore they exit column at different times. We refer to this type of transport as dispersed transport. We will now quantify these transport processes.

3.1. Advection

As we learned from our above experiment, advection (or also called convection) is the transport of matter or energy with the movement of a moving medium. The moving medium can be termed carrier, and in the groundwater case it is usually fluid. Convection is more frequently used with regard to energy or heat transport, while advection is more frequently used in the transport of matter. To quantify advection process, we will consider our laboratory column (Fig. 2) which has a constant cross-sectional area, A [L^2], the steady-state discharge, Q [L^3T^{-1}]. Further we will assume n_e [] the effective porosity of the column packing and v as average linear velocity of water flow. Note that $v = q/n_e$, where q is the Darcy velocity or also called specific discharge [LT^{-1}]. With these informations, we quantify the advective mass flow rate J_{adv} [MT^{-1}] as

$$J_{adv} = Q C \quad (1)$$

We may want to modify eq. (1) by considering the continuity equation in the column

$$Q = n_e A v = \text{constant} \quad (2)$$

Substituting eq. (2) in eq. (1), and defining advective flux, j_{adv} [$MT^{-1} L^{-2}$] = J_{adv}/A , we get

$$j_{adv} = J_{adv}/A = n_e v C \quad (3)$$

We have so far considered a uniform cross-section but because continuity equation has to be satisfied, it is not required that flow area remain uniform. This is better understood from Fig 3. Assuming that n_e is spatially constant, the mass (shown in grey patch) is the same in both flow sections. During the transition from the smaller to the larger cross-section, the area covered by the solute mass expands laterally and its extension along the flow direction is reduced accordingly, and therefore the concentration is not spatially changed.

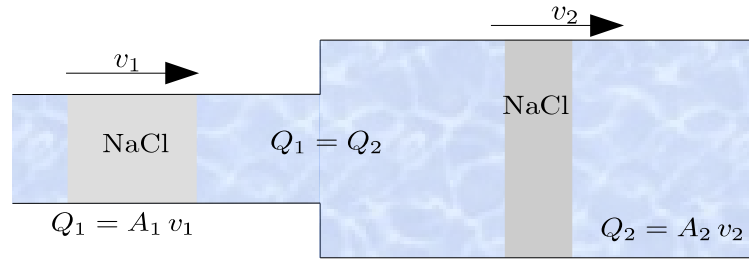


Fig. 3: Advection in a non-uniform cross-section

3.2. Mechanical Dispersion

We already know that spread of mass causes dispersion. Here we will first discuss the reasons behind the dispersion and then find a way to quantify it. As we will find later, spread of mass is not entirely a physical processes but physiochemical processes also causes spread. We refer mechanical dispersion to the spread due to physical processes only.

There is a general agreement in describing the mechanisms behind mechanical dispersion. The three most common mechanisms (also see Fig. 4) that can be found in standard literatures (*Freeze and Cherry, 1979, Domenico and Schwartz, 1998*) are:

- I. Non-uniform flow in an individual pore: From fluid mechanics it is know that a parabolic velocity profile results for a flow passing between two parallel solids (Fig. 4a). Thus mass passing through the centre line of the profile will be fastest and the one at the edge will be the slowest.
- II. Effect of Pore size distribution: Non-uniformity in pores size leads to different flow velocities with which the mass is transported in a wider pores (higher speed) compared to a narrower pores (Fig 4b).
- III. Effect of flow paths: Due to irregular distribution of pores in the porous media, mass particles are likely to take flow paths varying in lengths thus leading to meandering of particles (Fig 4c).

Next, we quantify dispersive mass flow rate, $J_{dis} [MT^{-1}]$ using our experiment (Fig 2). Quite clearly the last two mechanisms (point II and III, above) suggest that dispersion can be explained as a random phenomena, which are explained in standard texts, such as *Domenico and Schwartz, (1998)*. Based on observations, the dispersive mass flow due to mechanical dispersion in porous media is found to be

- I. proportional to the cross-sectional area, A , of the flow
- II. proportional to the linear velocity, v
- III. proportional to the difference in concentration at different location, $\Delta C = C_0 - C$
- IV. inversely proportional to the transport distance, L

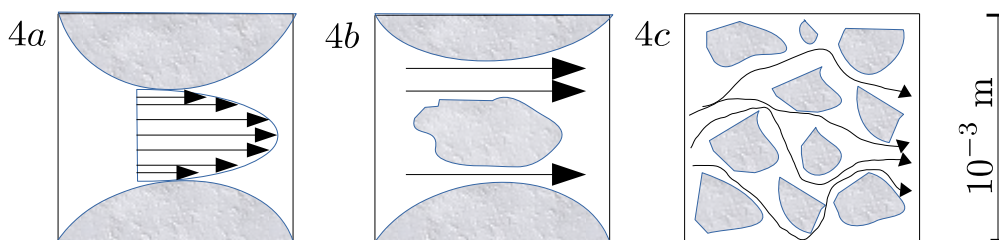


Fig. 4: The three mechanisms leading to dispersion (Adapted from *Kinzelbach, 1992*)

The four proportionality relations mentioned above lead to

$$J_{dis} \propto n_e A v \frac{\Delta C}{L} \quad (4)$$

which equates to

$$J_{dis} = -\alpha n_e A v \frac{\Delta C}{L} \quad (5)$$

with α a constant of proportionality called dispersivity [L]. The negative sign is used in equality relation to identify that transport is from a higher concentration towards the lower one. Dispersivity is a property of porous media alone and is not dependent on fluid type or the flow characteristics. In a more formal manner the ratio $\Delta C/L$ [ML⁻⁴] is termed as concentration gradient. This let us quantify dispersivity as a quantity whose value equals the dispersive mass flow rate through a unit cross-section area for a unit concentration gradient and a unit linear velocity.

As mass transport is influenced by both porous medium and flow properties, a product of dispersivity and linear velocity called the mechanical dispersion coefficient, D_{mech} [L²T⁻¹], is more often used in analysing dispersive transport. This changes eq. (5) to

$$J_{dis} = -D_{mech} n_e A \frac{\Delta C}{L} \quad (6)$$

with $D_{mech} = \alpha v$. Instead of mass flow rate one may use mass flux j_{dis} [MT⁻¹ L⁻²], which simply is

$$j_{dis} = \frac{J_{dis}}{A} = -D_{mech} n_e \frac{\Delta C}{L} \quad (7)$$

Since α characterizes spread length, its value is dependent on the flow coordinate direction under consideration. Furthermore, an excellent compilation and analysis by *Gelhar et al.*, (1992) shows a scale (travel distance) dependence of α . The compilation, which is highly referred, suggest the longitudinal α (along the direction of groundwater flow) varies between 10⁻³ m and 10³ m with bulk of values between 10⁻¹ m and 10² m. We will briefly discuss α values in transverse directions (horizontal and vertical) in the last topic of this section.

Advection and the mechanical dispersion are two processes that are generally used in analysing groundwater transport problems. Nevertheless, it is important for us to introduce a very important transport mechanism called diffusion that is not flow or mechanically driven but rather it is concentration gradient driven.

3.3. Diffusion

The quantification of diffusive mass transport, J_{dif} [MT⁻¹] is based on the work in *Fick*, (1855). In that work the mass flow due to diffusion (1D, Fig 2) is described to be

- I. proportional to the cross-sectional area of the flow, A
- II. proportional to the concentration difference between the transport distance, $\Delta C = C_0 - C$
- III. inversely proportional to the transport distance, L

The above three points are combined to constitute the Fick's first law of diffusion, which is

$$J_{dif} \propto A \frac{\Delta C}{L} \quad (8)$$

which equates to

$$J_{dif} = -D_{dif} A \frac{\Delta C}{L} \quad (9)$$

The negative sign in eq. (8) represents transport of mass from higher concentrations toward the lower one. D_{dif} [$L^2 T^{-1}$], is the constant of proportionality called diffusion coefficient. From eq. (9) we can get the diffusive flux j_{dif} [$MT^{-1} L^{-2}$] from

$$j_{dif} = \frac{J_{dif}}{A} = -D_{dif} \frac{\Delta C}{L} \quad (10)$$

Fick's law is based on studies of mass transport in free fluid. In groundwater transport the restriction to transport due to porous media (solid) has to be considered. This is appropriately represented by replacing D_{dif} with the pore diffusion coefficient, D_p , which is frequently quantified as

$$D_p = n_e D_{dif} \quad (11)$$

Tortuosity τ , which is the ratio between the effective (true) travel length (L_e) and the linear travel length (L), is another factor that is included in D_p quantification. The value of τ is reported (in Bear, 1972) to vary between 0.56 and 0.80. D_p is dependent on type of chemicals (ions) with value ranging between 10^{-8} and $m^2/s \cdot 10^{-10}$

It the analysis of groundwater transport problems the dispersion coefficient and the diffusion coefficient are summed and a new coefficient called hydrodynamic dispersion coefficient D_{hyd} is defined as in

$$D_{hyd} = D_{mech} + D_p = \alpha v + D_p \quad (12)$$

This summation is based on the fact that both dispersion and diffusion lead to spread of mass, and can be justified only on practical basis. It is to be noted that dispersion is physically driven process whereas difference is chemically driven process.

3.3. Joint Action of advection and Dispersion

The transport of conservative solute in an aquifer can be understood as a superposition of advection, mechanical dispersion and pore diffusion. To quantify the transported mass over the time, we sum all the mass flow rate, J [MT^{-1}] that we have considered. i.e., eqs. (1, 6 and 9). Thus we get a combined equation for the mass flow

$$J = J_{adv} + J_{dis} + J_{dif} = J_{adv} + J_{dis,h} \quad (13)$$

where $J_{dis,h} = J_{dis} + J_{dif}$ refer to mass flow due to hydrodynamic dispersion. Eq (13) can alternatively written as

$$= n_e A v C - n_e A D_{hyd} \frac{\Delta C}{L} J = n_e A v C - n_e A v \frac{\Delta C}{L} A D_p \frac{\Delta C}{L} \quad (14)$$

The spreading of mass due to advection and dispersion can be quantified by combining a mass budget and the corresponding laws of motion. This results in a transport equation called advection-dispersion or convection-dispersion equation, which we will be deriving and discussing in sections 4 and 5. The solution of the transport equation is given by the solute concentration that varies over time and space, i.e., $C(x, t)$.

With an example we will attempt to quantify the relative importance of different mass flow rate using eq. (14). Let us assume the following 1D column experiment:

Cross-section area of flow, $n_e A = 1 \text{ m}^2$

Linear velocity, $v = 1 \text{ m/d}$

Concentration, $C = 1 \text{ mg/L} = 1 \text{ g/m}^3$

Transport distance, $L = 1 \text{ m}$

Concentration gradient, $\Delta C/L = 1 \text{ g/m}^4$

Dispersivity, $\alpha = 0.1 \text{ m}$ ($\alpha = L/10$ is a rough estimate)

Diffusion coefficient, $D = 10^{-10} \text{ m}^2/\text{s}$

The contribution of advection can be obtained from eq. (1), we get

$$n_e A v C = 1 \text{ m}^2 \cdot 1 \text{ m/d} \cdot 1 \text{ g/m}^3 = 1 \text{ g/d}$$

likewise, the contribution of mechanical dispersion can be obtained from eq. (6), we get

$$n_e A v \alpha \Delta C/L = 1 \text{ m}^2 \cdot 0.1 \text{ m} \cdot 1 \text{ m/d} \cdot 1 \text{ g/m}^4 = 0.1 \text{ g/d}$$

and, similarly we can obtain the contribution of the pore diffusion from eq. (9)

$$n_e A D \Delta C/L = 1 \text{ m}^2 \cdot 10^{-10} \text{ m}^2/\text{s} \cdot 1 \text{ g/m}^4 = 10^{-10} \text{ g/d}$$

From the above example we can conclude that $J_{adv} > J_{dis}$ or a very rough estimate advection \approx dispersion, whereas $J_{disp} \gg J_{dif}$ or dispersion \gg diffusion. This example presents a typical case in unconsolidated aquifers. As such diffusion is very often neglected in the transport analysis. We still have to find a method to distinguish between the advective and the dispersive transport regimes. This can be achieved using the dimensionless number called Péclet number, which is given as

$$Pe = \frac{\text{transport by advection}}{\text{transport by diffusion}} = \frac{vd}{D_p} \quad (15)$$

in which $d [\text{L}]$ is mean grain diameter, and other quantities was defined earlier. As can also be observed in Fig. 5, the following three regimes are defined:

- I. For $Pe < 0.02$, diffusion dominates
- II. For $0.02 < Pe < 6$, diffusion and dispersion dominates
- III. For $Pe > 6$, advection and dispersion dominates

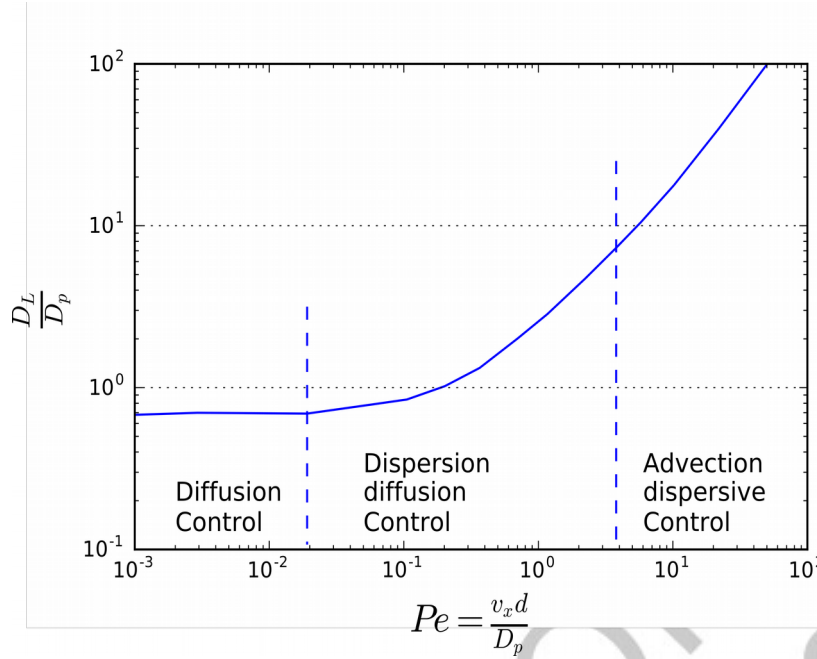


Fig. 5: Peclet number (Pe) and different transport regimes (adapted from Bear, 1972)

3.4. Visualizing and quantifying transport processes

Since advection is simply a transport along with groundwater flow, the advective mass at any point is the initial mass, and the position at any time instant t is the product of linear flow velocity, v , and t . This approach is used if advective mass flow is to be obtained in transverse directions. However, for most of the practical problems groundwater flow is considered unidirectional and along the horizontal direction. The quantification of dispersive mass flow, more often the dispersion/diffusion coefficients are rather complicated. We have already summed the two processes in eq. (12), furthermore we have hinted that these can be better described using statistical approach. In fact hydrodynamic dispersion coefficient (we will call it dispersion) has been related to a Gaussian distribution statistics as (see, *Domenico and Schwartz*, 1998)

$$\sigma = (2Dt)^{1/2} \quad (16)$$

where σ refers to square root of standard deviation or variance. If position is intended to be obtained, then t can be replaced with v/x . It is to be noted that eq. (16) represents the spatial (or space) distribution of the mass, but when mass evolution is to be obtained from temporal distribution, the following space-time interchange (from *Robbins*, 1989) has to be applied:

$$\sigma_L^2 = v^2 \sigma_t^2 \quad (17)$$

In this case σ_L^2 refers to variance from the spatial distribution where as σ_t^2 refers to variance from the temporal distribution. Dispersion coefficient can be computed by inverting eq (16 or 17). Thus we see two possibilities to visualize and analyse mass evolution and quantify parameters such as dispersion coefficients.

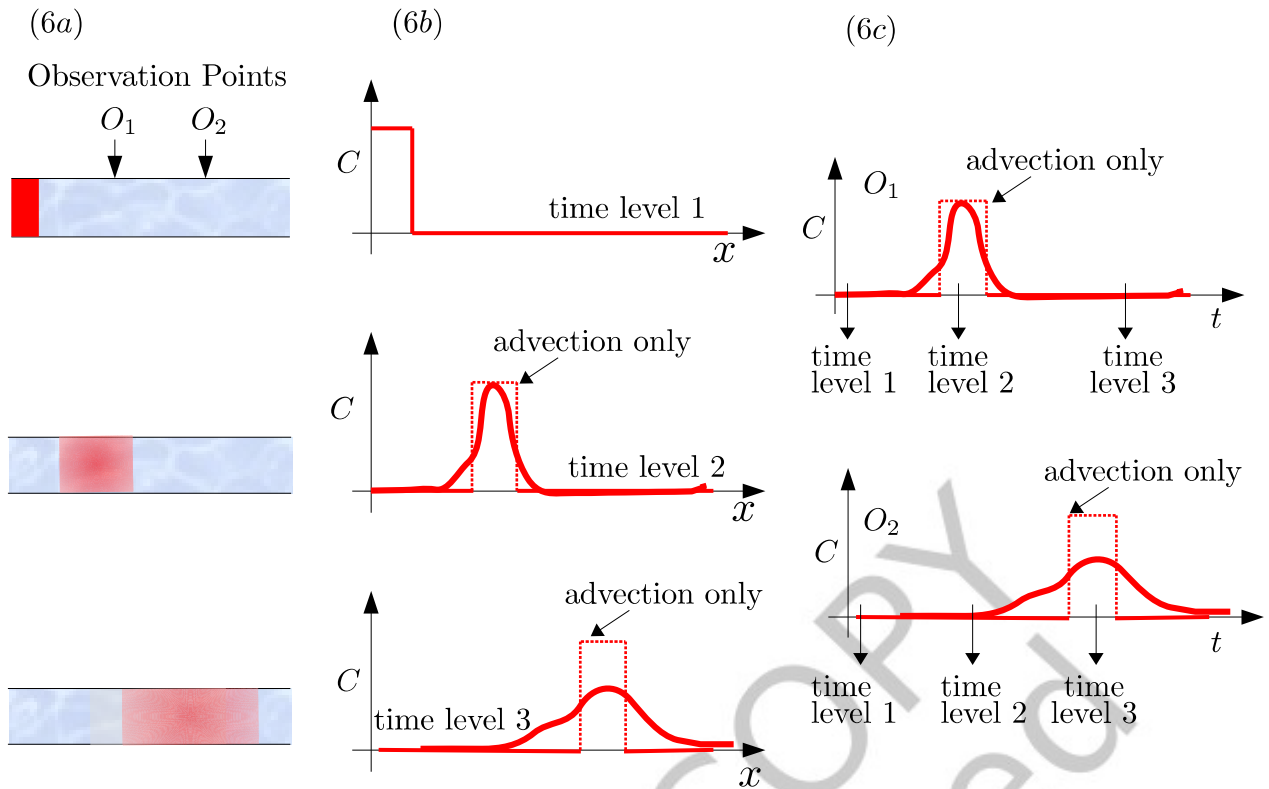


Fig 6: The evolution of mass in a 1D column (6a). The concentration profile (6a), and the breakthrough plot (6c)

Fig. 6 presents a schematic of mass evolution from a 1D column. As can be observed in the Fig 6c, breakthrough curves are representations of the solute concentration as a function of time at specified observation locations. Concentration profiles (Fig. 6b) are representations of the solute concentration as a function of a space coordinate at fixed time levels. Examples of using these plots for calculating dispersion coefficients can be found in *Levenspiel*, (1999), *Appelo and Postma*, (1999). Readers are encouraged to use an excellent spreadsheet that can simulate and plot breakthrough curves and concentration profile developed by Prof. J. Craig (Uni. Waterloo, Canada. <http://www.civil.uwaterloo.ca/jrcraig/pdf/OgataBanks.xlsm>).

Before we end the section, we briefly discuss the mass transport in 2D and 3D. While advective transport can essentially be 1D along groundwater flow, tedious efforts are required to understand and quantify dispersion coefficients in 2D and 3D, i.e., transverse dispersivities. We can extend our above discussions to quantify transverse dispersivities. As a rule of thumb, the horizontal transverse dispersivities (α_{Th}) can be assumed to be one-tenth of longitudinal dispersivity (α_L , that we have been discussing in this section) and, likewise, the vertical transverse dispersivity (α_{Tv}) can be approximated to be one-tenth of α_{Th} . These dispersivities are more relevant in reactive transport systems, which will discuss in the following sections.

4. Reactive Transport Processes

In the last section we distinguished between conservative and the reactive transport systems. Essentially, a reactive system is one in which the mass entering the domain undergoes changes resulting to either increase or decrease of the original mass. Both cases are possible due to some form of chemical reactions taking place within the domain. This change in mass has to be accounted in the transport system, which so far for us includes advection and dispersion processes. Thus we are now exploring a very broad topic on aquatic chemistry. For this introductory module, we will restrict to the three different types of aquatic reactions namely: sorption, decay and degradation. In the next section we will learn about combining the conservative and reactive components of transport systems.

4.1. Equilibrium Sorption

In the study of groundwater, at least at the introductory level, we use a common term sorption for adsorption and absorption. By sorption, we will actually be learning on adsorption reaction. To begin let us start with common terminologies. Adsorption is the process of accumulation of dissolved chemicals on the surface of a solid, e.g. accumulation of a chemical dissolved in groundwater on the surface of the aquifer materials. In most cases, adsorption is a reversible process, i.e. adsorbed chemicals can become dissolved again. This process is termed desorption. Two components of adsorption-desorption are adsorbent and adsorbate. The first one is the solid offering adsorption sites and the latter one is the chemical that get accumulated on the adsorbent. Interactions between adsorbent and adsorbate depend on properties of both substances. Fig. 7 presents a schematic representation of a sorption process along with its various components.

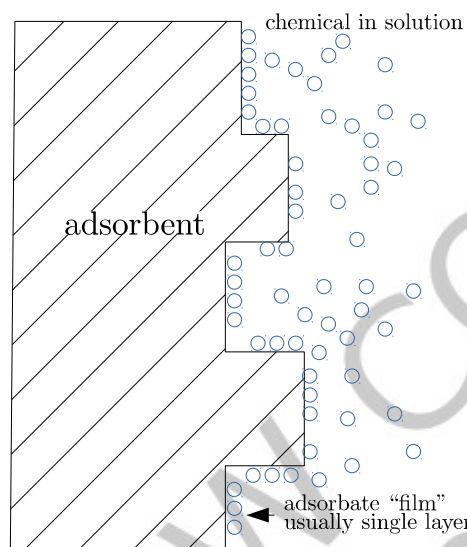


Fig 7: The sorption components

An equilibrium between the adsorbent and adsorbate on the surface and in the solution is approached with time. The equilibrium condition can be used to quantify the sorption process. The so-called isotherms, which provide a relationship between the solute concentration $C [ML^{-3}]$ in the dissolved phase and the adsorbate mass to adsorbent mass ratio $C_a []$. The concept of isotherms is derived from the Chemical Engineering studies, which provide several different types of isotherms. In groundwater transport problems Linear, Freundlich and Langmuir isotherms are the common ones. Next we will learn about these isotherms.

4.1.1. The Linear isotherm

The Linear isotherm also called the Henry isotherm or the K_d model is based on the linear relationship between C and C_a . Mathematically it is represented by

$$C_a = K_d C \quad (18)$$

in which $K_d [L^3 M^{-1}]$ is called the distribution or portioning coefficient. Although simple but this isotherm has several limitations. Among the most important ones are that this isotherm assumes that sorption is unlimited, i.e., an adsorbent has infinite number of sites for sorption. More often in groundwater transport problems the available number of sites are not a limiting factor, however that linearity is always followed may not be the case. Largely because of its mathematical simplicity (linearity), the linear isotherm is extensively used in analysing groundwater transport problems (see *EPA*, (1999) for further learning). Let us

perform a simple experiment to obtain a in the laboratory. Let us equilibrate six different concentrations (C_i , mg/L) of a solute in six different flasks each with 10 g of an identical adsorbent. The results of the experiment is presented in Table 1. We then plot the C_a (mg/g) against C (mg/L) and linearly fit the data. The slope of the fit, which is 1.404 is the K_D (see Fig. 8)

Table 1: Different concentrations from hypothetical experiment to find K_D

Initial C_i	Equilibrium C	C_a
50	15	35
75	30	45
100	40	60
150	60	90
200	0	120
250	100	150

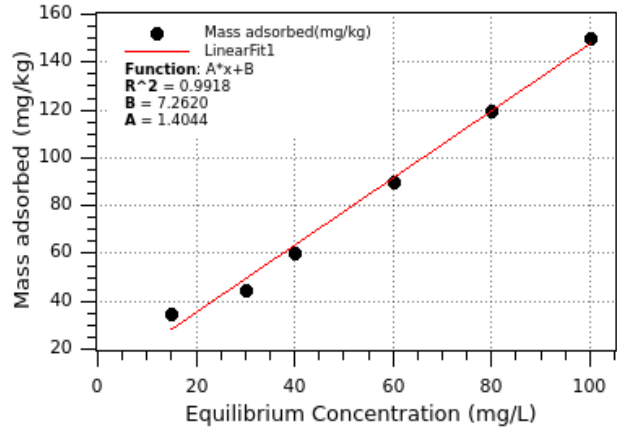


Fig. 8: Obtaining K_D from the experimental results

4.1.2. The Langmuir isotherm

The main limitation of the linear isotherm that the absorbent has infinite capacity to adsorb is avoided in the Langmuir isotherm. This is achieved based on the assumptions that ions are adsorbed as a monolayer on the surface, and the maximum adsorption occurs when the adsorbent surface is completely occupied by the adsorbate. Mathematically the Langmuir isotherm is

$$C_a = \frac{C_{a,m} K_L C}{1 + K_L C} \quad (19)$$

in which $K_L [L^3 M^{-1}]$ is the Langmuir coefficient and $C_{a,m}$ is the maximum number of ions that can be adsorbed on the surface. As we did previously, we will perform a hypothetical experiment to estimate $C_{a,m}$ and obtain K_L . In this experiment we will add 250 mg/L of solute to six flasks containing different amounts of absorbent. The experiment results and calculations are tabulated in Table 2. Fig. 9 presents the plot of results in which the $C_{a,max}$ is found approximately at 0.1 mg/mg. We are still required to find K_L . This will require fitting the data that we have in Fig. 9. Although it is possible to fit the results plot with eq. (19), a much simpler approach is to linearise the equation. This is easily achievable by first inverting both side of eq. (19) and rearranging. The linearised form of eq (19) is

$$\frac{1}{C_a} = \frac{1}{C_{a,m}} + \frac{1}{K_L C_{a,m}} \cdot \frac{1}{C} \quad (20)$$

By comparing the linear fit equation (see right plot Fig. 9) of experimental results with eq. (20), both $C_{a,m}$ and K_L can be easily obtained. Inverting the intercept of the fit line provides $C_{a,m}$ and then K_L can be obtained by equating the slope of the fit with $1/(K_L C_{a,m})$

Table 2: Different concentrations from our hypothetical experiment to obtain $C_{a,m}$ and K_L

Initial C_i (mg/L)	Adsorbent mass (mg/L)	C (mg/L)	C_a (mg/mg)	$1/C$ (L/mg)	$1/C_a$ (mg/mg)
250	804	4.7	49.06	0.213	0.061
250	668	7	48.6	0.143	0.073
250	512	9.31	48.1	0.107	0.094
250	393	16.6	46.68	0.060	0.119
250	313	32.5	43.5	0.031	0.139
250	238	62.8	37.44	0.016	0.157

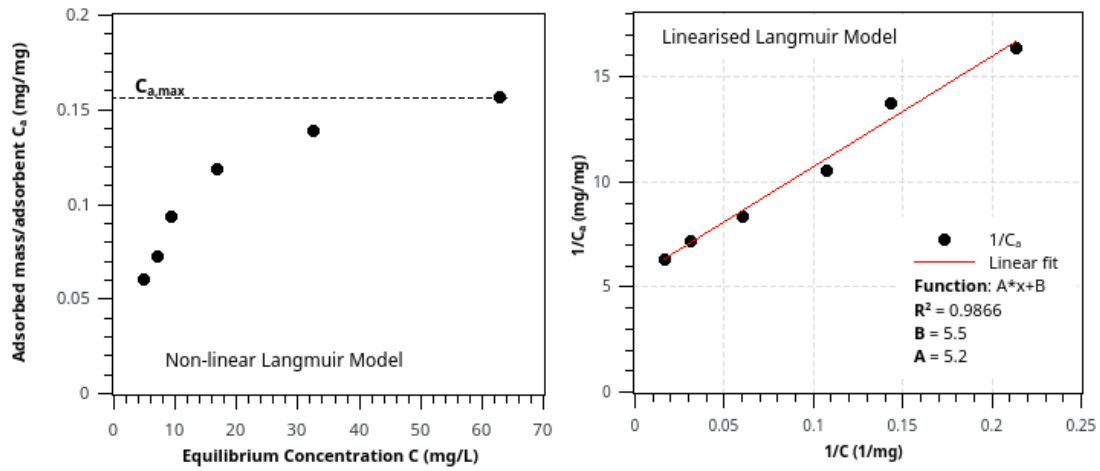


Fig 9: The Langmuir isotherm(left plot) and its linearised form (right)

4.1.3. Freundlich isotherm

The Freundlich isotherm is a modified form of K_D model and it observes the non-linearity involved with sorption process. It is based on the idea of a power law relating the C and C_a . The isotherm is given as

$$C_a = K_F C^n \quad (21)$$

in which K_F is the Freundlich constant and n is the measure of the non-linearity involved. As is with the K_D model, the Freundlich isotherm is not able to provide any information on maximum possible sorption.

The Freundlich isotherm becomes equivalent to K_D model for $n = 1$. For illustration and obtaining K_F and the value of n , we will work on a similar experiment that we performed for the demonstrating Langmuir isotherm (see Table 13, and Fig. 9). As we did earlier we will linearise eq. (21), and then use a linear fit to obtain the K_F and n from fit parameters. Taking a logarithm (base 10) on both side of eq. (21) and using the properties of logarithm, we can linearise it. The linearised form of eq. (21) is

$$\log C_a = \log K_F + n \log C \quad (22)$$

Fig. 10 and Table 3 (below) illustrates the processes for obtaining K_F and n using eq. (21) and eq. (22). From the analysis we see that $K_F = 0.023$ and $n = 0.62$.

4.1.4. Retardation factor

The most significant effect of the sorption is that it leads to retardation of the mass being transported. This basically means that mass will be transported slower than the average groundwater velocity. The coefficient of retardation R is used to estimate retarded contaminant velocity. We first derive R and then find the retarded mass velocity. For this purpose we will use our above discussion on linear isotherm (or K_D model). Further we will apply mass balance equation.

Let us assume aquifer of volume V with an effective porosity n_e and material density ρ . Thus we have:

total water volume: $n_e V$

mass of dissolved chemical: $n_e V C$

volume of solid: $(1 - n_e) V$

mass of solid: $\rho(1 - n_e)V$

mass of adsorbate: $\rho(1 - n_e)V C_a = (1 - n_e)\rho V K_D C$

Total mass: $n_e V C + (1 - n_e)\rho V K_D C = n_e R V C$

with $R = 1 + \frac{1 - n_e}{n_e} \rho K_D$. Using bulk density (mass of solid/total volume) $\rho_b = (1 - n_e)\rho$, R becomes

$$R = 1 + \frac{\rho_b K_D}{n_e} \quad (23)$$

Table 3: Different concentrations from hypothetical experiment to find K_D

C	C_a	$\log C$	$\log C_a$
3.5	0.05	-1.3	0.54
5.2	0.06	-1.19	0.72
8	0.08	-1.08	0.90
12.5	0.11	-0.96	1.10
20.5	0.15	-0.82	1.31
33	0.2	-0.7	1.52

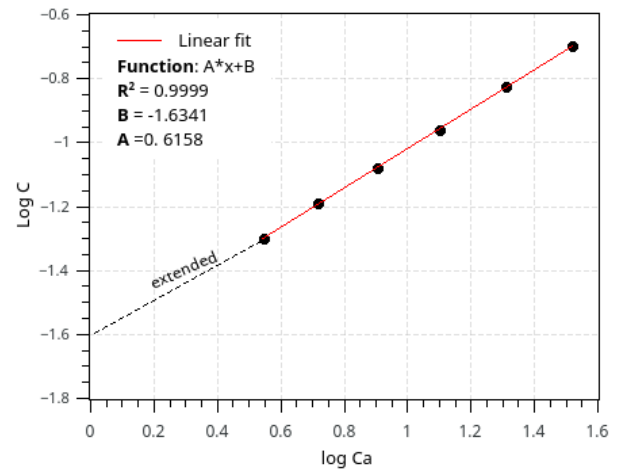


Fig. 10: Linearised Freundlich Isotherm

With R known the retarded velocity $V_m [LT^{-1}]$ of the mass can be obtained from

$$R = \frac{v}{v_m} \quad (24)$$

4.2. Chemical Degradation

Degradation includes all reactive processes which eventually lead to the removal of chemical from the aquifers. This is in contrast to sorption/desorption processes which only lead to a transfer or partition of the chemical between adsorbent and the solution. In essence degradation results to breaking of the chemical structure of the mass whereas the same remains intact in the sorption process. If mass toxicity is an issue under consideration, it has to be noted that chemical destruction do not guarantee that the new chemical formed (daughter products) are less toxic.

Time-dependent degradation or concerning reaction kinetics are common in the mathematical formulation of transport problems that include chemical degradation. A general equation of reaction kinetics is

$$\frac{dC}{dt} = -\lambda C^n \quad (25)$$

with t time, C solute concentration, n [·] the order of degradation kinetics ($n \geq 0$) and λ the degradation rate constant. The unit (and the dimension) of λ depends on the order of the reaction kinetics. Assuming that initial or at $t = 0$ concentration of C in the aquifer is C_0 , solution of eq. (25) are

$$C(t) = C_0 \exp^{-\lambda t} \text{ if } n = 1 \quad (26)$$

and

$$C(t) = [C_0^{1-n}(1-n)\lambda]^{-\frac{1}{1-n}} \text{ if } n \neq 1 \quad (27)$$

For degradation kinetics of order $n \geq 1$ the solute concentration asymptotically approaches zero and for the case $n < 1$ the solute concentration actually reaches zero. Decay (a form of degradation, e.g., radioactive decay) obeys a first-order rate law. Quite often half life $t_{1/2}$ is used in explaining the degradation kinetics. $t_{1/2}$ refers to the time span elapsing until the initial concentration C_0 is reduced by half. With exception of $n = 1$ case, the $t_{1/2}$ depends on the initial concentration in nearly all cases. Let us illustrate the decay case with an example. Table 4. presents a Cobalt 60 and Strontium 90 decay data over the time. The first order fit (eq. 26) of the data is provided in Fig. 11. Readers are suggested to explore a spreadsheet (nth-order.ods, Open office format) originally developed by Prof. R. Liedl (TU Dresden, Germany), which can be found at <https://github.com/prabhasyadav/UGC-Transport> for exploring further the different orders of decay fit. With known $t_{1/2}$, which is 5.26 y and 28 y for Cobalt 60 and Strontium 90, respectively, the rate constant (λ) for the first order decay equation (eq. 26) can be obtained from

Table 4: Cobalt and Strontium isotope decay

Time (y)	Cobalt 60 (mg/L)	Strontium 90 (mg/L)
0	10	10
1	8.76	9.76
2	7.68	9.52
5	5.17	8.84
10	2.68	7.81
20	0.72	6.1
28	0.25	5

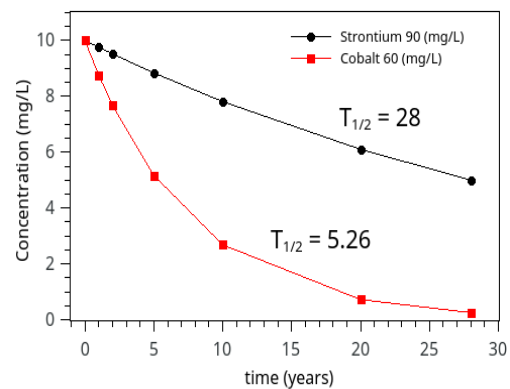


Fig 11: First order fit for Cobalt 60 and Strontium 90 decay

$$\lambda = \frac{\ln(2)}{t_{1/2}} \quad (28)$$

For our example problem, the decay constants are thus 0.025 1/y and 0.132 1/y for Cobalt 60 and Strontium 90, respectively. The zeroth-order ($n = 0$) and the first order ($n = 1$) decay equations are more commonly found to fit with transport problems. One can use the spreadsheet (mentioned above) for checking different orders of decay equation. Fig 12 presents the zeroth-order and the first order results obtained from the spreadsheet.

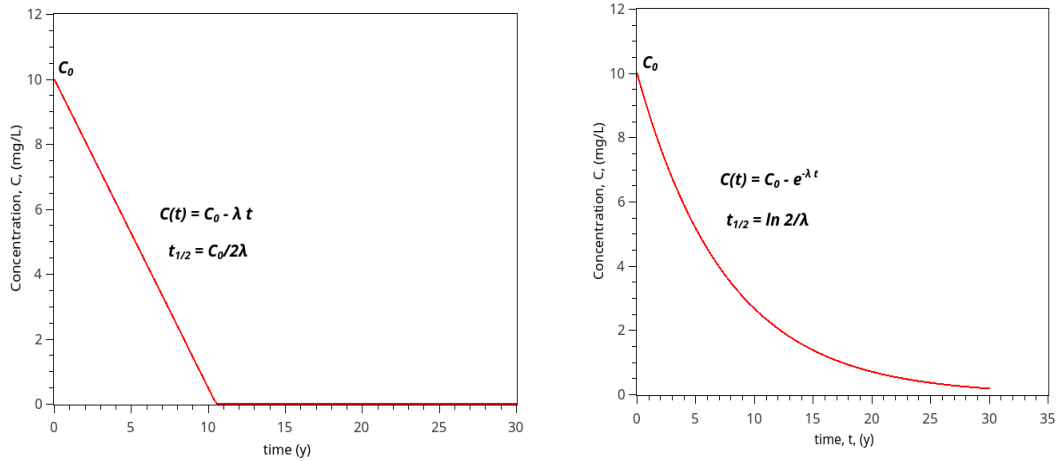


Fig 12: The zero order (left) and the first order decay curve (right).

These plots can be obtained from the spreadsheet.

4.3. Biological Degradation

Microbially mediated degradation are common in aquifers. The degradation processes can include mineralization, in which organic compounds are converted to inorganic compounds; detoxification, in which toxic chemicals are transformed to non-toxic compounds; and cometabolism, in which a compound is fortuitously degraded by an enzyme or cofactor produced during microbial metabolism of another compound. The most common mathematical formulation of microbially mediated degradation is the one presented by *Monod*, (1949), which is also called Monod or Michaelis-Menten kinetics. The formulation is

$$\frac{dC}{dt} = \mu_m \frac{C}{K_c + C} \quad (29)$$

where μ_m [T^{-1}] is maximum growth rate, C [$M L^{-1}$] is mass concentration (also called substrate) and K_c the half saturation constant, which allows the microbes to grow at half the maximum specific growth rate. Eq. (29) contains region of zero-order kinetics (for short times) and the region of first-order kinetics (for long times). When $C \gg K_c$, $K_c + C \approx C$, and eq. (29) approaches zero-order with

$$\frac{dC}{dt} = \mu_m \quad (30)$$

and μ_m becomes the limiting maximum reaction rate. When $C \gg K_c$, eq. (29) reduces to

$$\frac{dC}{dt} = \frac{\mu_m}{K_c} C \quad (31)$$

and the reaction approaches the first order, with μ_m/K_c equal to the first-order rate constant. Assuming C_0 , as an initial concentration an implicit solution of eq. (29) is

$$t = \frac{C_0 - C(t)}{\mu_m} + \frac{K_c}{\mu_m} \ln \frac{C_0}{C(t)} \quad (32)$$

and the half life $t_{1/2}$ is given by

$$t_{1/2} = \frac{C_0}{2\mu_{max}} + \frac{K_c}{\mu_{max}} \ln 2 \quad (33)$$

Fig. 13 presents a plot of eqs. (30, 31 and 32). A spreadsheet (monod.ods) has been developed (Open office format, <https://github.com/prabhasyadav/UGC-Transport>) that can be used to interactively simulate and visualise the Michaelis-Menten kinetics. Readers are encouraged to use it.

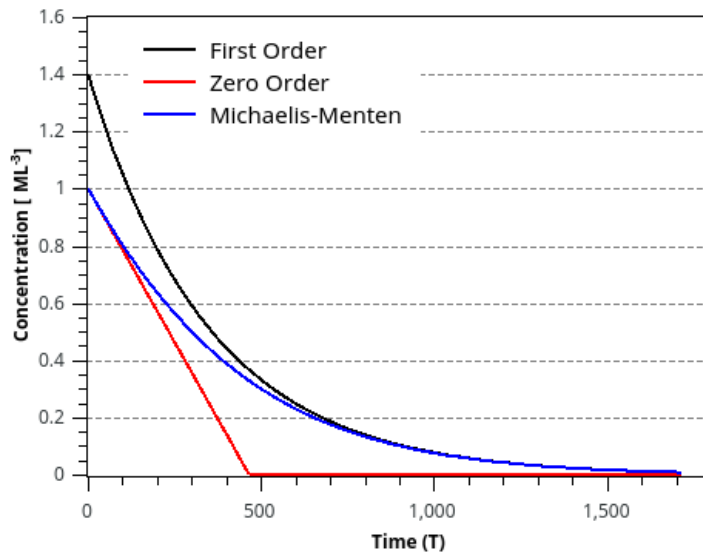


Fig. 13: plot of zero-order, first-order and the Michaelis-Mention kinetics

5. Transport Models

So far our discussions have been focussing on processes involved in mass transport in aquifers. We have attempted laboratory based experiments (and some mathematical steps) to obtain parameters required for quantifying different processes of the transport. In these attempts we quantified processes separately, but in the natural transport problems several processes affect the system simultaneously (Fig. 14). Thus our next step will be to combine several processes and attempt a solution of such system. Clearly, we are now moving towards mathematical realm of transport problems. In this section we will first derive a $2D$ differential statement of the transport problem with fewer reactive components and subsequently we will explore the various complexities of the problem. We will also explore conditions (initial and boundary) required to solve the problem and end by generalizing the transport equation.

5.1. Derivation of transport model

Transport equations are derived by using a representative control volume (or RCV see Fig 1). For the transport problems ($2D$), the RCV extends from the aquifer bottom to the aquifer top in confined aquifers.

In an unconfined aquifers the RCV extends from the aquifer bottom to the groundwater table. Furthermore average concentration along the thickness is used. The fundamental transport equation is based on mass balance relation and laws of motion used in advection and dispersion. To these we add equations of reactive processes when reactive transport model is to be obtained. For the derivation we will consider a 2D transport in the horizontal (xy -plane) with advection along the x -axis. The groundwater flow is steady, i.e., v_x is constant. we will consider 2D dispersion and additionally we will include injection of the mass at the rate, E , (wells). For the reactive part we will consider sorption represented by the K_D model (eq. 18) and chemical degradation, D , using first-order kinetics (eq. 26). The mass balance equation in the RCV is then (see Fig. 15 next page)

$$\frac{\Delta M}{\Delta t} = J_{in} - J_{out} + E - D \quad (34)$$

Where ΔM is change in mass in the RCV over time Δt . For deriving the transport equation, we will have find an expression for each term of eq. (34). The mass of a chemical in a RCV is distributed between the dissolved phase C , i.e., in flowing water and sorbed to the solid matrix, C_a . Let n_e be the porosity of RCV then we have:

- I. The volume of the RCV, $V = \Delta x \Delta y m$
- II. The dissolved mass, $= n_e V C$
- III. The sorbed mass $= V \rho_b C_a = V \rho_b K_d C$ (ρ_b is bulk density, see eq. 23)
- IV. The total mass, M , in RCV $= \text{II} + \text{III}$, which is:

$$M = n_e V C + V \rho_b K_d C = n_e (1 + \rho_b K_d / n_e) V C = n_e R V C$$

in which n_e , R and V are fixed quantities, then the change of mass ΔM over time Δt is given as

$$\Delta M = n_e R V \Delta C = n_e R \Delta x \Delta y m \Delta C \quad (35)$$

with ΔC being the change in solute concentration. Since the RCV is very small compared to the actual study area, the components of mass flux ($j = J/A$) can be assumed to change linearly across the extension of a RCV. These changes are obtained by multiplying first-order derivatives with corresponding distances, i.e., using Taylor series expansion (see Fig. 16). We thus get

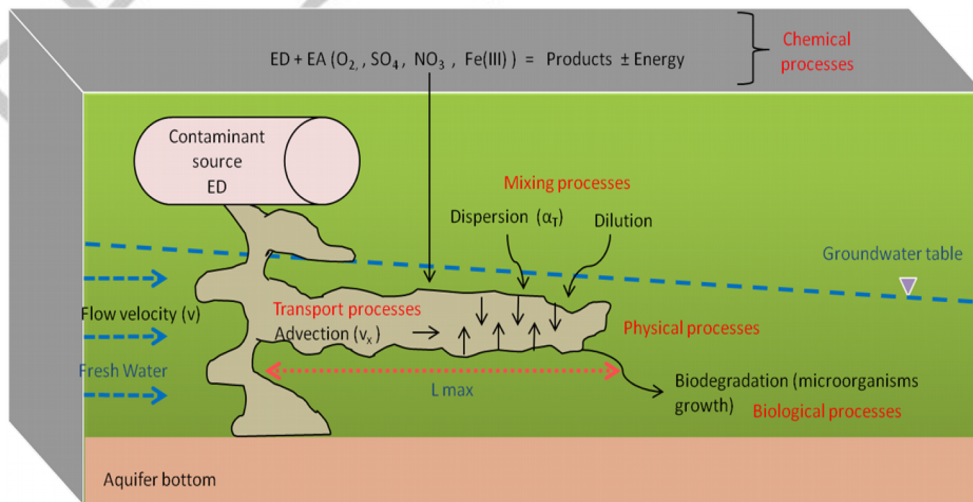


Fig 14: A schematic figure portraying different processes of a transport problem

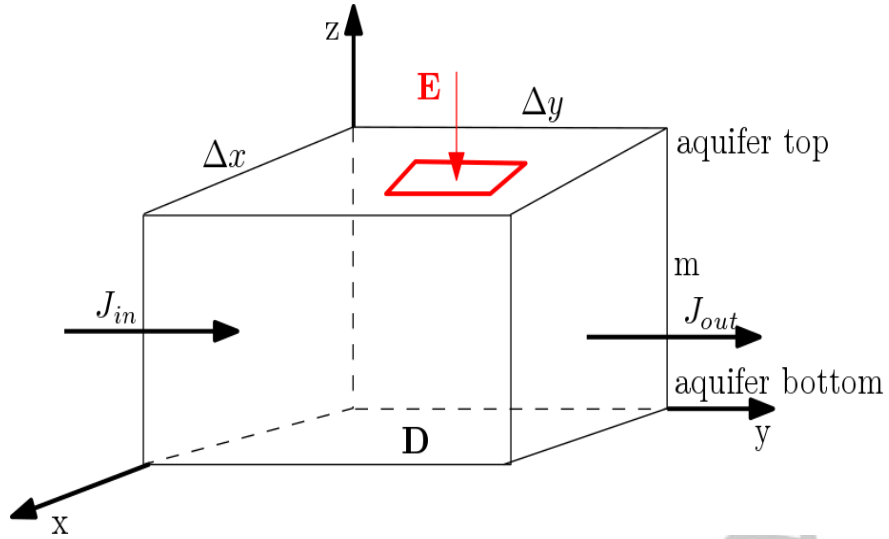


Fig 15: A RCV with different mass components

with ΔC being the change in solute concentration. Since the RCV is very small compared to the actual study area, the components of mass flux ($j = J/A$) can be assumed to change linearly across the extension of a RCV. These changes are obtained by multiplying first-order derivatives with corresponding distances, i.e., using Taylor series expansion (see Fig. 16) . We thus get

$$J_{in} = j_x m \Delta y + j_y m \Delta x \quad (36)$$

and

$$J_{out} = \left(j_x + \frac{\partial j_x}{\partial x} \Delta x \right) m \Delta y + \left(j_y + \frac{\partial j_y}{\partial y} \Delta y \right) m \Delta x \quad (37)$$

and the difference is

$$J_{in} - J_{out} = -\frac{\partial j_x}{\partial x} m \Delta x \Delta y - \frac{\partial j_y}{\partial y} m \Delta x \Delta y \quad (38)$$

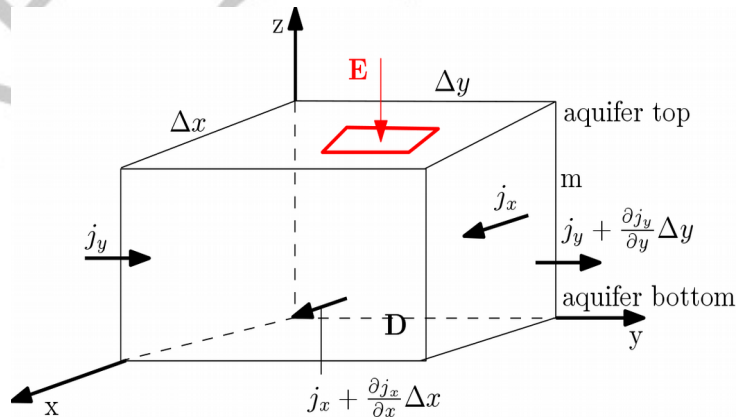


Fig. 16: Fluxes in a RCV

Let us first finalize the results obtained so far neglecting E and D . Inserting the expressions for ΔM (eq. 57) and $(J_{in} - J_{out})$ (eq. 38) in eq. (34), we get

$$n_e R \Delta x \Delta y m \frac{\Delta C}{\Delta t} = -\frac{\partial j_x}{\partial x} m \Delta x \Delta y - \frac{\partial j_y}{\partial y} m \Delta x \Delta y \quad (39)$$

Cancelling common factors and letting $\Delta t \rightarrow 0$ in eq (39) changes it to

$$n_e R \frac{\partial C}{\partial t} = -\frac{\partial j_x}{\partial x} - \frac{\partial j_y}{\partial y} \quad (40)$$

Let us now consider degradation, which results to loss of mass in the control volume. For our case we will assume that degradation is only taking place in dissolved phase. Further, we are considering the first-order degradation kinetics, i.e. $n = 1$ in eq. (25). The temporal change of dissolved mass is therefore given by

$$n_e \frac{\partial C}{\partial t} = -\lambda n_e C \quad (41)$$

n_e is added in the above equation in order to represent the degradation in the dissolved phase only. Eq. (41) has to be added to the right hand side of eq. (40) to include the contribution of degradation in the mass balance within the RCV. Thus we get

$$n_e R \frac{\partial C}{\partial t} = -\frac{\partial j_x}{\partial x} - \frac{\partial j_y}{\partial y} - \lambda n_e C \quad (42)$$

Let us now inject mass to the RCV. For that we will consider a volumetric flow rate per unit area $N [LT^{-1}]$. Using N we can calculate

- I. The total volume of water injected V_w at $\Delta t = N \Delta x \Delta y \Delta t$
- II. The injected mass $E \Delta t = N \Delta x \Delta y \Delta t C_E$

with C_E being the concentration at the time instant of measurement in RCV. The transport equation we have (eq. 42) so far represents the mass change in a unit volume (reference volume, V) as such the expression for E has to be per unit volume when it is to be included in the transport equation, i.e. we need E/V . The right hand side of point II can then be written as

$$E \Delta t = N \Delta x \Delta y \Delta t C_E = N \frac{V}{m} \Delta t C_E$$

which in terms of E/V becomes

$$\frac{E}{V} = \frac{N}{m} C_E \quad (43)$$

To complete our transport equation we add eq. (43) to the right hand side of eq. (42), then we get

$$n_e R \frac{\partial C}{\partial t} = -\frac{\partial j_x}{\partial x} - \frac{\partial j_y}{\partial y} - \lambda n_e C + \frac{N}{m} C_E \quad (44)$$

The process we have adopted to develop the transport equation indicates that other processes when required can simply be added to the equation. Finally to complete our transport equation we will use laws of motion to replace fluxes (j_x and j_y). For this we will use eq. (14), which provide the mass flow rate ($J = jA$) due to advection and dispersion. For the $2D$ case for the flow in parallel to the x -axis, the fluxes can be represented in matrix form as

$$\begin{pmatrix} j_x \\ j_y \end{pmatrix} = n_e \cdot \begin{pmatrix} v_x \\ 0 \end{pmatrix} \cdot C - n_e \cdot \begin{pmatrix} \alpha_L v_x & 0 \\ v_x & \alpha_{Th} v_x \end{pmatrix} \cdot \begin{pmatrix} \frac{\partial C}{\partial x} \\ \frac{\partial C}{\partial y} \end{pmatrix}$$

which represents the following set of equations.

$$j_x = n_e v_x C - n_e \alpha_L v_x \frac{\partial C}{\partial x} \quad (45)$$

and

$$j_y = -n_e \alpha_{Th} v_x \frac{\partial C}{\partial y} \quad (46)$$

Note that we have use $D_{hyd} = \alpha v$ in the above equations. We will insert eqs. (45 and 46) to complete our transport equation (eq. 44), thus we get

$$\begin{aligned} n_e R \frac{\partial C}{\partial t} = & - \frac{\partial}{\partial x} \left(n_e v_x C - n_e \alpha_L v_x \frac{\partial C}{\partial x} \right) - \frac{\partial}{\partial y} \left(- n_e \alpha_{Th} v_x \frac{\partial C}{\partial y} \right) - \\ & - \lambda n_e C + \frac{N}{m} C_E \end{aligned} \quad (47)$$

If we let n_e be constant it can be taken out of differentials, consequently eq. (47) after rearrangement becomes

$$R \frac{\partial C}{\partial t} + \frac{\partial}{\partial x} (v_x C) = \frac{\partial}{\partial x} \left(\alpha_L v_x \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left(\alpha_{Th} v_x \frac{\partial C}{\partial y} \right) - \lambda C + \frac{N C_m}{n_e m} \quad (48)$$

Eq. (48), a $2D$ transport equation, can be converted to $1D$ transport equation by removing the y -components and likewise it can be converted to $3D$ transport equation by adding the z -components. We explain these when we generalize the transport equation in the end of the section. Next we learn about other essential requirements for transport problems.

5.2. Initial and boundary conditions

A transport model does not only consist of the transport equations. A complete set of transport problem includes the transport equation, e.g., eq. (48), the initial conditions (time dependent) and the boundary conditions (space dependent). The initial condition describes the distribution of mass or specifies concentration in the entire area of investigation at some starting time, usually $t = 0$ is considered. The initial conditions are required for the transport problems that are time dependent (e.g., eq. 48). These are so called transient problems and they comprise of general transport problems. A mathematical statement of initial condition is

$$C(t = 0) = C_0 \quad (49)$$

i.e., at $t = 0$, C_0 is the concentration in the entire investigated area.

For time-independent problems, i.e., $\partial C / \partial t = 0$, also called steady-state problems boundary conditions are required to be specified. The boundary conditions quantify the impacts of condition at the surrounding just adjacent to the area under investigation. As the name suggests, the boundary conditions have to be specified for the entire boundary of the investigation area, even for the cases when the investigated area in unlimited or extend are infinite. The boundary conditions may or may not be time dependent. For transport problems three types of boundary conditions have been defined.

A first type of boundary condition, also called Dirichlet type, specifies the value of mass or concentration at the boundary. The mathematical statement of the first type boundary condition is

$$C(x, y, z, t) = C_0 \quad (50)$$

i.e., at any t , the concentration at specified space (x, y, z) is C_0 . Tracer injection, effluent concentration from polluted area can be few examples of first type boundary conditions. In a second type boundary condition, also called Neumann type condition, the component of the concentration gradient perpendicular to the boundary is specified. The mathematical statement of the second type boundary condition along x -axis is

$$\frac{dC(t)}{dx} = C_0 \quad (51)$$

Since the gradient of concentration is proportional to diffusive flux, the second type boundary condition is also called a flux specified boundary. Second type boundary conditions are also used for specifying the no-flow condition, i.e., no concentration gradient exist across the boundary. However it has to be noted that absolute no-flow can only exist when there is no concentration gradient and the velocity vector is zero. Rock formation at the bottom of aquifer will result to a no flow type of boundary condition.

The third type, Cauchy or Robin type, conditions combines the first two conditions, i.e. both a specific value and gradient is specified. This condition generalizes the other two boundary conditions. Mathematical statement of the third type boundary condition (along x -axis) is

$$\frac{dC(t)}{dx} + C(x, t) = C_0 \quad (52)$$

5.3. Generalization of transport models

Transport problem that we derived in section 5.1 can be considered as a simplified general problem. In a natural setting transport problems can be very complex. The complexities arises from scenarios such as

- I. Requiring a 3D investigation
- II. Problems with temporally and spatially variable linear velocity
- III. Problems requiring non-linear equilibrium isotherms (e.g., Freundlich) or non-equilibrium sorption.
- IV. Problems requiring higher order degradation kinetics or Monod kinetics.
- V. Multi-species problems and multiple simultaneous reactions.

These more general problems are described by adding their expressions to the transport equation, as was done in section 5.1., or the problems can be represented by system of equations. As the complexity of a problem increases, the number of parameters and the initial and boundary conditions required to be specified also increases. As an example we discuss the effect of variable linear velocity in the transport problem.

Let us start by re-stating eq. (48) which we derived for a flow in parallel with the x -axis, i.e., $v_x = \text{constant}$ and $v_y = 0$

$$R \frac{\partial C}{\partial t} + \frac{\partial}{\partial x}(v_x C) = \frac{\partial}{\partial x} \left(\alpha_L v_x \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left(\alpha_{Th} v_x \frac{\partial C}{\partial y} \right) - \lambda C + \frac{N C_m}{n_e m}$$

If in the above equation, linear velocity is a variable then the y -component has to be considered in the advective term (the second term on the left hand side). This simply requires adding a y -component as is done

for the x -component. But now the dispersion too depends on v_y and in this case the dispersion matrix for flow in parallel with the x -axis is

$$D = \begin{pmatrix} D_{xx} & D_{xy} \\ D_{yx} & D_{yy} \end{pmatrix} = \begin{pmatrix} \alpha_L v_x & 0 \\ 0 & \alpha_{Th} v_x \end{pmatrix}$$

is expanded according to (from Bear 1972)

$$D = \begin{pmatrix} D_{xx} & D_{xy} \\ D_{yx} & D_{yy} \end{pmatrix} = \frac{1}{|v|} \cdot \begin{pmatrix} \alpha_L v_x^2 + \alpha_T v_y^2 & (\alpha_L - \alpha_{Th}) v_x v_y \\ (\alpha_L - \alpha_{Th}) v_x v_y & \alpha_L v_y^2 + \alpha_T v_x^2 \end{pmatrix} \quad (53)$$

with $|v| = \sqrt{v_x^2 + v_y^2}$. Thus the 2D transport equation for variable linear velocity becomes

$$\begin{aligned} R \frac{\partial C}{\partial t} + \frac{\partial}{\partial x}(v_x C) \frac{\partial}{\partial y}(v_y C) = \\ = \frac{\partial}{\partial x} \left(D_{xx} \frac{\partial C}{\partial x} + D_{xy} \frac{\partial C}{\partial y} \right) + \frac{\partial}{\partial y} \left(D_{yx} \frac{\partial C}{\partial x} + D_{yy} \frac{\partial C}{\partial y} \right) - \lambda C + \frac{N C_m}{n_e m} \end{aligned} \quad (54)$$

This equation contains two advective terms and four dispersive terms. In case the 3D analysis is required we will have three advective terms and up to nine dispersive terms. In the same way the transport problem can be of reduced complexity, then to what we have derived and discussed so far. For example a 1D column can be described by one advective term and one dispersive term. In addition we usually have $N = 0$ in the laboratory columns. The equation in that case is

$$R \frac{\partial C}{\partial t} + \frac{\partial}{\partial x}(v_x C) = \frac{\partial}{\partial x} \left(\alpha_L v_x \frac{\partial C}{\partial x} \right) - \lambda C \quad (55)$$

with $D = \alpha v$. A much simpler problem will appear if steady-state can be considered. In that case eq. (55) will be a second order linear ordinary differential equation. In the next section we will attempt to solve the transport problems.

6. Solving Transport Problems

In the previous sections we learned about the transport problems and developed the transport equation, also called Advection-Dispersion-Reaction (ADR) equation. In this section we will attempt to solve the ADR model, which has been one of our objective from this module. The techniques for solving the transport problems are extremely varied and therefore we will restrict to simpler problems (1D, and few reaction components etc.). We will very briefly get introduced to complex problems (higher dimensions, multiple reaction).

Direct integrating of the ADR equation (e.g. eq. 47) is only possible in very simplified cases (e.g., only advection case). However, transformation methods (Laplace, Fourier etc.) can be applied to directly solve ADR equation under some conditions. Thus obtained solutions are called analytical models, which are exact and often a closed-form. The conditions very generally include that aquifer is of regular geometry, is homogeneous and isotropic and the chemical reactions are linear models based. Numerical methods, e.g. Finite-Difference Method (FDM), Finite-Element Method (FEM), that provide approximate solution of the ADR equation are very commonly used to solve transport problems. In this module we will restrict to few analytical model and very briefly discuss numerical methods.

6.1. Few analytical solutions

The solution provided in the succeeding subsections generally assumes the following:

1. Fluid of constant density and viscosity
2. Flow in x -direction only, and velocity is constant.
3. The longitudinal dispersion coefficient D_x is constant.

In addition we assume aquifer is homogeneous and isotropic. Additional assumptions is provided when required.

6.1.1. The Adevection-Dispersion (AD) equation

The simplest ADR equation can be a transient 1D equation without the reaction term, i.e. AD equation, which is

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (56)$$

we consider the initial condition

$$C(x, t = 0) = C_0$$

and boundary conditions

$$C(x = 0, t) = C_{in} \quad \text{and} \quad c(x = \infty, t) = 0$$

The conditions implies that our investigation area is semi-infinite and contain C_0 concentration initially and C_{in} concentration is continuously injected to the investigation area from the location $x = 0$. The following analytical solution of this problem is provided in *Ogata and Banks, (1961)*:

$$C(x, t) = C_0 + \frac{C_{in} - C_0}{2} \left(\operatorname{erfc} \left(\frac{x - vt}{2\sqrt{Dt}} \right) + \exp \left(\frac{v}{D} x \right) \operatorname{erfc} \left(\frac{x + vt}{2\sqrt{Dt}} \right) \right) \quad (57)$$

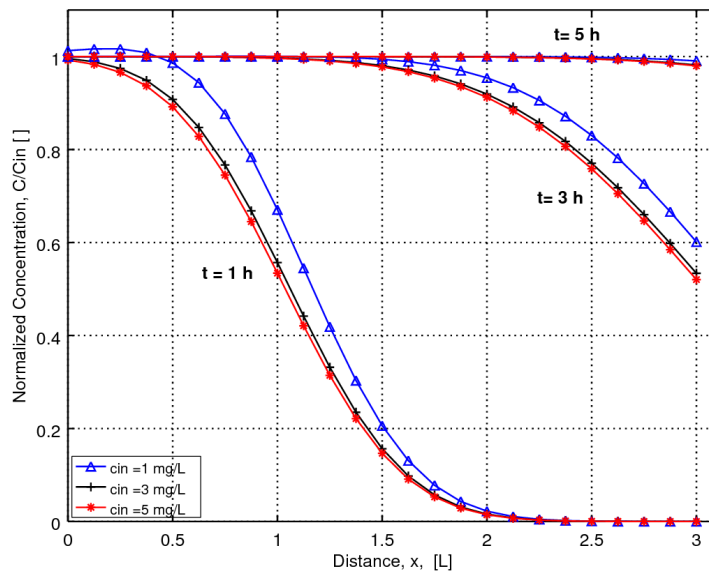


Fig. 17: Visualizing the Ogata and Banks (1961) solution

in which erfc denotes the complementary error-function, which is defined as

$$\text{erfc}(x) = 1 - \text{erf}(x) \text{ with } \text{erf}(x) = \frac{1}{\sqrt{\pi}} \int_{-x}^x e^{-t^2} dt$$

Readers should check the wikipedia site (https://en.wikipedia.org/wiki/Error_function) to find methods to approximate the value of erfc .

In order to visualize eq. (69) we perform a column (3 m long) experiment with $C_0 = 0$ mg/L, $v = 1$ m/h and $D = 1$ m²/h. Let our $C_{in} = 1, 3$ and 5 mg/L. We will check the concentration in the column at different times. Fig. 17 provides the results of our experiment. The result suggest that it will require 5 hours for our homogeneous distribution of mass in the column. For further visualisation of the Ogata and Banks solution, readers may check the GNU-Octave (open source computing system similar to MATLAB®: <https://www.gnu.org/software/octave/>) code (ogata1D.m) provided at <https://github.com/prabhasyadav/UGC-Transport>.

6.1.2. The AD equation with first-order decay

We now increase the complexity our transport problem by including the first-order decay term. In that case eq. (69) becomes

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \lambda C \quad (58)$$

we will consider the initial condition

$$C(x, t = 0) = 0 \text{ with } 0 < x < \infty \quad (59)$$

and boundary conditions

$$C(x = 0, t) = C_{in} \text{ and } C(x = \infty, t), \frac{\partial C(x = \infty, t)}{\partial x} = 0 \quad (60)$$

An analytical solution of the above transport problem is provided by Wexler (1992) as

$$C(x, t) = \frac{C_{in}}{2} \left[\left(\exp \left(\frac{x}{2D} (v - u) \right) \text{erfc} \left(\frac{x - ut}{2\sqrt{Dt}} \right) + \exp \left(\frac{x}{2D} (v + u) \right) \text{erfc} \left(\frac{x + ut}{2\sqrt{Dt}} \right) \right] \quad (61)$$

with $u = \sqrt{v^2 + 4\lambda D}$. To visualize the solution we will continue with our previous experiment letting $D = 0.1$ m²/h and $C_{in} = 1$ mg/L. Fig. 18 provides the result of our experiment, in which we see the concentration distribution at $t = 1$ h at different location of the column. For comparison purpose we have simulated the $\lambda = 0$ in one case, which is equivalent to the solution in eq. (69), and several other values of λ . Readers can experiment further with the solution using the GNU Octave code (decay1D.m) provided at the site: <https://github.com/prabhasyadav/UGC-Transport>.

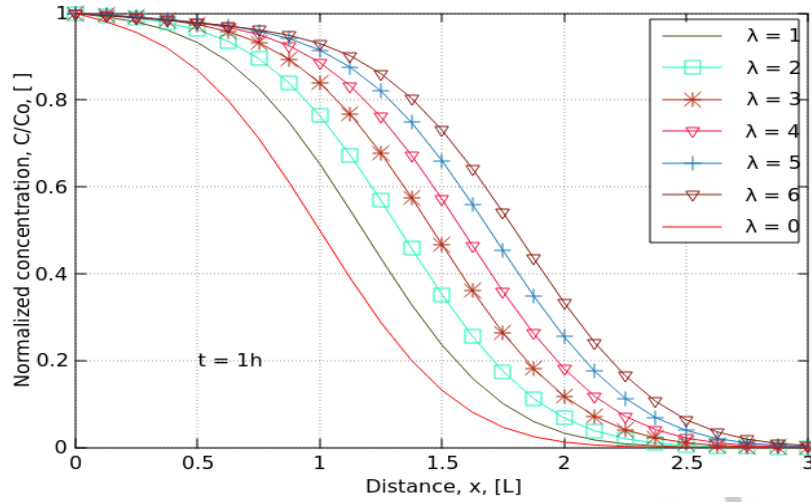


Fig 18: Comparing different values of λ using Wexler (1992) solution. $\lambda = 0$ refers to AD model

6.1.3. The AD equation with first-order decay and linear sorption

Our next step will be to introduce sorption to our transport equation. In this case our transport equation becomes

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \lambda C \quad (62)$$

with initial and boundary conditions provided in eqs. (59 and 60). For this problem the following analytical solution is provided in Kinzelbach, (1992)

$$C(x, t) = C_0 \exp(-\lambda t) \left[1 - \frac{1}{2} \operatorname{erfc} \left(\frac{Rx - vt}{2\sqrt{D R t}} \right) - \frac{1}{2} \exp \left(\frac{v x}{D} \right) \operatorname{erfc} \left(\frac{Rx + vt}{2\sqrt{D R t}} \right) \right] + \frac{C_{in}}{2} \left[\exp \left(\frac{v - u}{2D} x \right) \operatorname{erfc} \left(\frac{Rx - ut}{2\sqrt{D R t}} \right) + \exp \left(\frac{v + u}{2D} x \right) \operatorname{erfc} \left(\frac{Rx + ut}{2\sqrt{D R t}} \right) \right] \quad (63)$$

with $u = \sqrt{v^2 + 4 \lambda R D}$. We can use our previous experiment to visualise the solution. It is noted that $R = 1$ refers to no sorption condition and we can simulate truly sorption case using eq. (63) by letting $\lambda = 0$ and $R > 1$. Note that when $C_0 = 0$, i.e., when no mass is present in the domain initially, eq. (63) contains terms that are a product of C_{in} only. The results of the experiment where we have let $D = 0.1 \text{ m}^2/\text{h}$ and $C_{in} = 1 \text{ mg/L}$ are presented in Fig. 19. Cases that the figure presents are, concentration at different periods, effect of λ , effect of different R , joint effect of R and λ . Using the GNU Octave code (retard1D.m, see <https://github.com/prabhasyadav/UGC-Transport>), readers can analyse scenarios not provided in Fig. 19.

In the above discussions we have limited to a single set of initial and boundary conditions. For a different conditions, we will have different analytical solutions. Genuchten and Alves, (1982), Kinzelbach, (1992), Wexler, (1992) provide excellent collection of analytical solutions for transport models with varieties of initial and boundary conditions. Readers are suggested to check these works for advancing their knowledge.

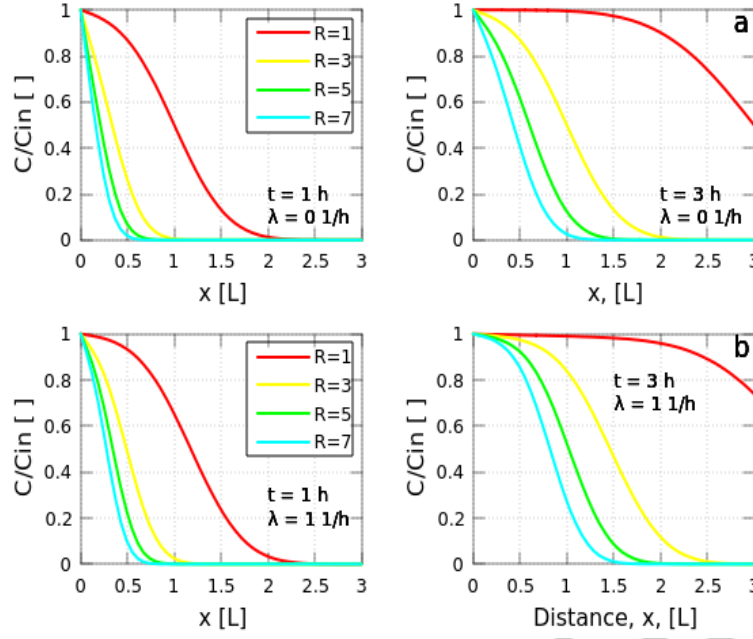


Fig 19: Visualizing transport model with decay and sorption using analytical solution from Kinzelbach (1992).

6.1.4. The 2D and 3D transport problems and their solution

We now focus on analytical models for higher dimensions (2D and 3D). For higher dimensions we will use the concept of Gaussian models, which are based on normal distribution function $f(x)$ given as

$$f(x) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2\right) \quad (64)$$

The normal distribution function $f(x)$ with $\mu = 0$ and $\sigma = \sqrt{2Dt}$ is the solution of the transport equation

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} D \frac{\partial C}{\partial x} \quad (65)$$

which is a dispersion equation. For this solution the required initial condition we require pulse type injection (infinite concentration) located at a very small area (at $x = 0$). This type of condition is termed as Dirac function (or δ -function), which is defined by the following two properties:

$$\delta(x) = \begin{cases} \infty & \text{for } x = 0 \\ 0 & \text{for } x \neq 0 \end{cases} \quad \text{and} \quad \int_{-\infty}^{\infty} \delta(x) dx = 1 \quad (66)$$

The solution of diffusion equation (eq. 65) can be extended to include the advective term, i.e., the AD equation in 1D. In that cases eq. (64) becomes

$$C(x, t) = \frac{M}{\sqrt{4\pi D t}} \exp\left(-\frac{(x - vt)^2}{4 t D}\right) \quad (67)$$

in which M is the total mass per unit area. To visualise the solution, we consider an example with $D = 0.625 \times 10^{-2} \text{ m}^2/\text{d}$, $v = 0.1 \text{ m/d}$ for different t . The results are presented in Fig. 20. Note that the

area under each curve is and it represents the total mass injected to the system. Further analysis of the system is easily possible using the code `inst1D.m` provided at: <https://github.com/prabhasyadav/UGC-Transport>.

The 1D analysis can be extended to the 2D and 3D cases. In these cases the 1D normal distribution (eq. 64) is generalized for 2D as

$$f(x, y) = \frac{1}{\sqrt{2\pi\sigma_x\sigma_y}} \exp \left(-\frac{1}{2} \left[\left(\frac{x - \mu_x}{\sigma_x} \right)^2 + \left(\frac{y - \mu_y}{\sigma_y} \right)^2 \right] \right) \quad (68)$$

with σ_x and σ_y the standard deviations and μ_x and μ_y the means in x - and y - directions, respectively. As with 1D, the dispersion coefficients can be related to standard deviation as $\sigma_x = \sqrt{2D_x t}$ and $\sigma_y = \sqrt{2D_y t}$. In a similar the boundary condition (eq. 66) can be adopted for the 2D case.

For the 2D case the *Kinzelbach*, (1992) provide an analytical solution for the transport problem that also include the first-order decay. The solution is

$$C(x, y, t) = \frac{M}{4\pi t \sqrt{D_x D_y}} \exp \left(-\frac{1}{4t} \left(\frac{(x - vt)^2}{D_x} + \frac{y^2}{D_y} \right) - \lambda t \right) \quad (69)$$

We will continue with the example problem that we started in our 1D problem. The additional data we use are $D_x = 0.01 \text{ m}^2/\text{d}$, $D_y = 0.625 \times 10^{-2} \text{ m}^2/\text{d}$ and $\lambda = 0 \text{ 1/d}$, i.e., no degradation case. Concentration contour is more appropriate for visualizing the results of 2D problems. Fig. 21(top, in the next page), presents the concentration contour for our example problem for $t = 1 \text{ d}$. Additionally, 2D surface plot (Fig. 21, bottom) can also be used for visualization of 2D problems. These plots can be generated using Octave code `transport2D.m`, which can be obtained from <https://github.com/prabhasyadav/UGC-Transport>. The code can be used for the further analysis of the problem, e.g., effect of different λ values, dispersion coefficients.

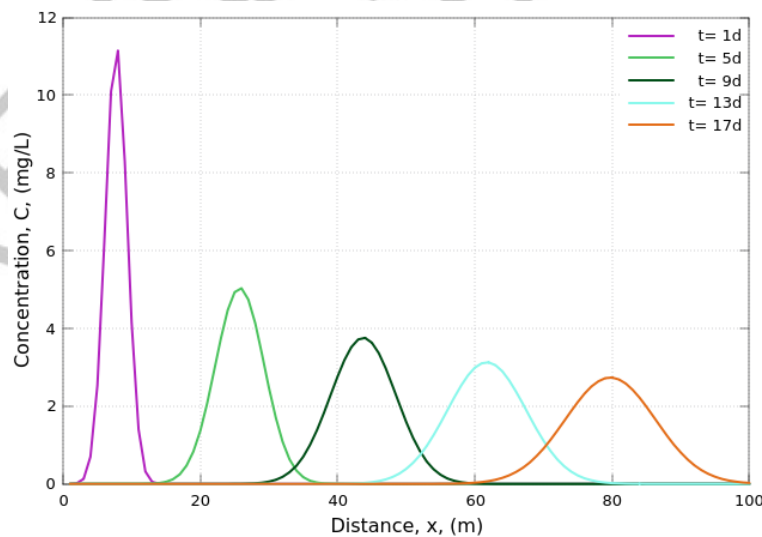


Fig 20: 1D transport for pulse-type source at different times.

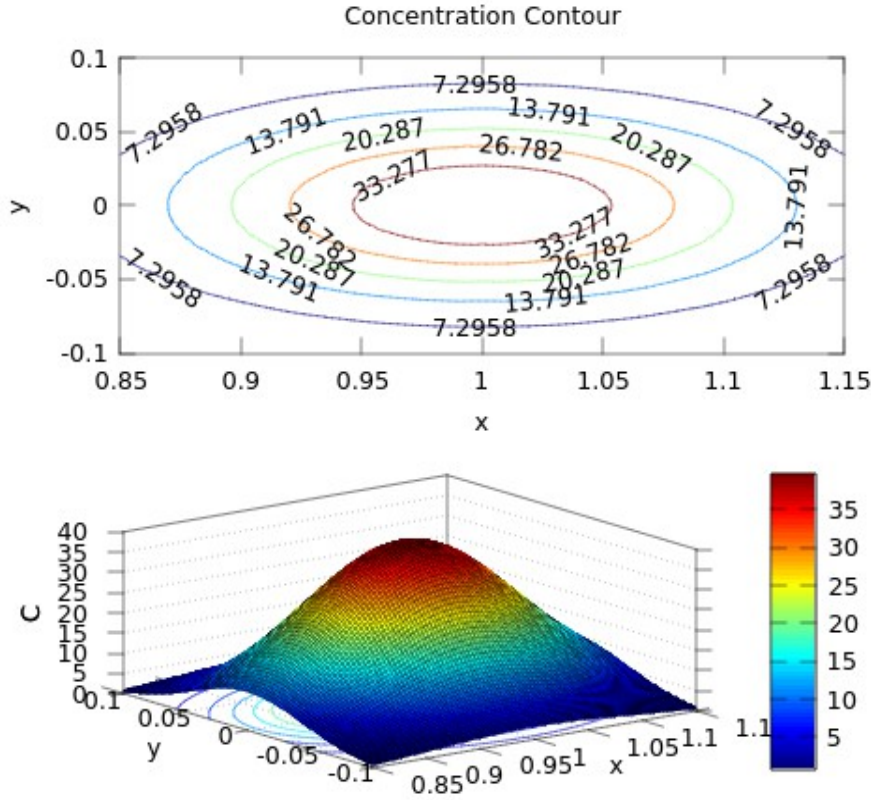


Fig 21: Visualizing the 2D transport problem at $t = 1$ d. Concentration contour is provided in the top plot and the surface plot at the bottom.

The solution of the 3D transport problem can be analogously obtained from the 2D solution. In this case we will have three dispersion terms. The solution to a 3D problem with first-order decay is provided by *Wexler*, (1992) as

$$C(x, y, z, t) = \frac{M}{(\sqrt{4\pi t})^3 \sqrt{D_x D_y D_z}} \exp \left(-\frac{1}{4t} \left(\frac{(x - vt)^2}{D_x} + \frac{y^2}{D_y} + \frac{z^2}{D_z} \right) - \lambda t \right) \quad (70)$$

Visualizing 3D transport problems are challenging and we consider that beyond our scope.

6.2. An introduction to numerical method for transport problems

Numerical modelling is generally used for solving transport problems. The main reason behind this is that analytical solution are possible for only few cases, often limited to regular domain geometry and linear (differential) equations. These limitations are easily overcome by numerical method. This topic is a very extensive. Here, we intend to only introduce the topic very briefly. Among few numerical methods that are available, Finite Difference Method (FDM) and Finite Element Method (FEM) are the two very extensively used in solving transport problems. We will focus on these two methods. Towards the end of the section we will use an example problem to illustrate FDM, the more common of the two methods mentioned above.

In the FDM the governing partial differential equation is replaced by a set of difference equations applicable to the system of nodes, i.e., the area under investigation is discretized into structured meshes. Taylor series expansion or polynomial fitting techniques are used to approximate all space/time derivative in terms of concentration. For example the first and second order derivatives of the transport equation is approximated using

$$\left(\frac{\partial C}{\partial x}\right)_i \approx \frac{C_{i+1} - C_{i-1}}{2\Delta x} \quad (71)$$

and

$$\left(\frac{\partial^2 C}{\partial x^2}\right)_i \approx \frac{C_{i+1} + 2C_i - C_{i-1}}{(\Delta x)^2} \quad (72)$$

where i refers to the node i and $i + 1$ and $i - 1$ are two adjacent nodes. Δx represents the width of the node, which may be a constant. A system of algebraic equations results when each node in the domain is considered. The system of equations is then solved using matrix algebra techniques. The most important aspect of FDM is the ease of formulating difference equations. *Anderson and Woessner*, (1992) provides an excellent introduction to the method. Readers are suggested to start with that literature if interested in learning the FDM for groundwater studies. For modelling, MODFLOW (an open-source) developed and maintained by United States Geological Survey (USGS) can be considered academic, research and industry standard. Interested individuals are suggested to explore MODFLOW at <http://water.usgs.gov/ogw/modflow/>.

The mathematics of FEM is not as straightforward as that of FDM. In this method the area under investigation is subdivided into elements that are defined by nodes. The element can be of different shapes, although triangular and quadrilateral shapes are the most common one used. Generation of FEM mesh is very tedious, as such FEM codes usually include mesh generation software. The solution of the differential equation using FEM is found as a combination of shape functions. The shape function (also called Lagrangian function) for the triangular element are linear within each element. Thus in Cartesian coordinates the shape function f is

$$f(x, y) = a_{\alpha 0} + a_{\alpha 1}x + a_{\alpha 2}y \quad (73)$$

within element α . All coefficients $a_{\alpha j}$ for all elements are computed, which is derived from the integral equivalent of differential equation, also called weak formulation (*Huyakorn and Pinder*, 1983).

6.2.1. An example numerical solution

As an illustration we use FDM to solve a transport problem. The first step is to develop a conceptual model (Fig. 22). In our example a 2D homogeneous, isotropic aquifer is considered. The problem has two flow components the horizontal (groundwater flow) and vertical over-flow. Two reactive masses (electron acceptor and electron donor) enters the domain (investigated area) through different flow directions. Fig. 22 (left) presents the conceptual model.

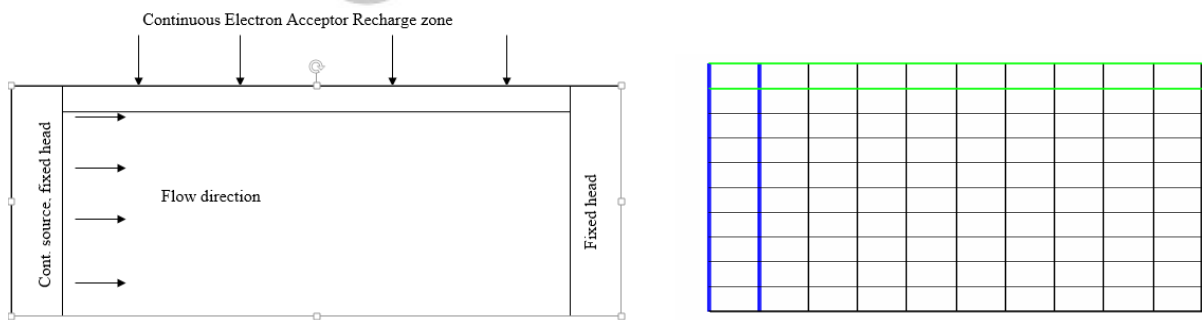


Fig 22: The conceptual model (left) and the discretized model (right)

The next step is to discretize the model domain. In case of FDM this can be simple rectangular boxes. Fig. 22 (right) presents the discretized domain. This step is critical as both large and very small sized grid can result to large error in approximation of the solution. The next step is to assign initial and boundary conditions to the model problem. In this problem first-type boundary conditions ($C(x, t) = C_0$) are used on the left, top and right ($C_0 = 0$, at infinite distance) of the domain, whereas no-flow boundary or second type boundary ($dC/dx = 0$) is assigned at the bottom. Once the boundary conditions are assigned, the other domain parameters are assigned. These can include conductivity, porosity etc. The final step is to select the transport model parameters. For transport problems these include dispersion coefficients, reaction parameters. Fig. 23 presents the solution of a problem that was obtained using MODFLOW. Interested reader can use the model input file (modell.gpt) from <https://github.com/prabhasyadav/UGC-Transport> to explore the example problem and the numerical method.

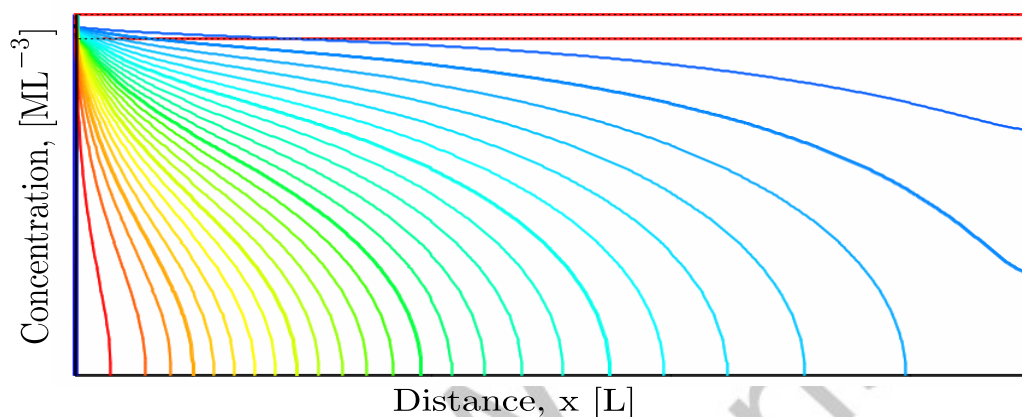


Fig 23: The concentration contour of the example problem.

7. Summary

The goal of the module is to introduce the groundwater transport problem, which is key to analysing, quantifying and solving the groundwater quality problems. The target groups are senior UG students and junior PG students. The module takes a systematic approach in first introducing the physical transport problems using a non-reactive mass transport system, also called conservative system. With this system the processes such as advection (flow induced transport), dispersion (spread of mass due to physical properties of aquifer and flow dynamics, and diffusion (concentration gradient induced transport) are introduced, mathematically formulated and compared.

In the reactive transport, chemical and biological processes that affect the transport of the mass in the aquifer are explained. In detail and with examples, chemical processes such as sorption (different isotherms-Linear, Langmuir and Freundlich) and decay kinetics of different orders are explained. Further spreadsheets have been developed for further analysis of the processes.

Transport models, the Advection-Dispersion-Reaction (ADR) equation is derived after understanding the sound knowledge of transport processes. For clarity and easier understanding 1D ADR equation is derived combining the reactive and conservative processes of mass transport. For completing the understanding, 2D and 3D dimensional problems are briefly introduced.

The last section of the module introduces techniques to solve the transport problems. The focus here has been 1D problems. Several analytical solution of transport problems are presented and visualized with an example. GNU Octave (MATLAB like open-source software) code have been developed for different types of transport equation, i.e, conservative type, reactive type with decay only and reactive type with decay and sorption. The codes are used for visualising the results. For complementing the understanding, numerical methods (Finite Difference and Finite-Element) are introduced.

The module encourages use of computing resources for understanding, analysing and exploring transport problems. For that matter a dedicated website: <https://github.com/prabhasyadav/UGC-Transport> provides codes, graphics and additional documents for advancing knowledge on topics covered in the module.

8. References

1. Anderson, M. P., and W. W. Woessner (1992), *Applied groundwater modeling: simulation of flow and advective transport*, Academic Press, San Diego.
2. Appelo, C. A. J., and D. Postma (1999), *Geochemistry, groundwater and pollution*, Balkema, Rotterdam.
3. Domenico, P. A., and F. W. Schwartz (1998), *Physical and chemical hydrogeology*, Wiley, New York.
4. EPA (1999), *Understanding variation in partition coefficient, K_d , values*, U.S. Environmental Protection Agency.
5. Fick, A. (1855), Ueber Diffusion, *Ann. Phys. Chem.*, 170(1), 59–86, doi:10.1002/andp.18551700105.
6. Freeze, R. A., and J. A. Cherry (1979), *Groundwater*, Prentice-Hall, Englewood Cliffs, N.J.
7. Gelhar, L. W., C. Welty, and K. R. Rehfeldt (1992), A critical review of data on field-scale dispersion in aquifers, *Water Resour. Res.*, 28(7), 1955–1974, doi:10.1029/92WR00607.
8. Genuchten, M. T. van, and W. J. Alves (1982), *Analytical solutions of the one-dimensional convective-dispersive solute transport equation*, U.S. Department of Agriculture.
9. Huyakorn, P. S., and H. R. Pinder (1983), *Computational methods in subsurface flow*, Elsevier Science, Oxford.
10. Kinzelbach, W. (1992), *Numerische Methoden zur Modellierung des Transports von Schadstoffen im Grundwasser*, Oldenbourg, München.
11. Levenspiel, O. (1999), *Chemical reaction engineering*, 3rd ed., Wiley, New York.
12. Monod, J. (1949), The Growth of Bacterial Cultures, *Annu. Rev. Microbiol.*, 3(1), 371–394, doi:10.1146/annurev.mi.03.100149.002103.
13. Ogata, A., and R. B. Banks (1961), *A solution of the differential equation of longitudinal dispersion in porous media*, U.S. Geological Survey.
14. Robbins, G. A. (1989), Methods for determining transverse dispersion coefficients of porous media in laboratory column experiments, *Water Resour. Res.*, 25(6), 1249–1258, doi:10.1029/WR025i006p01249.

15. Wexler, E. (1992), Analytical solutions for one-, two-, and three-dimensional solute transport in groundwater systems with uniform flow, in *Techniques of Water-Resources Investigations of the United States Geological Survey*, p. 190.

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