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Transport of Reacting Solutes in Rivers and Streams

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U. S. Geological Survey

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Introduction

In this chapter we discuss the major processes affecting solutes in rivers and streams. Here a *solute* is generally defined as any substance or entity that is transported downstream by the flowing waters. Under this definition, solutes may be pollutants, such as pesticides and hydrocarbons, or naturally occurring substances such as dissolved gases, nutrients, and trace elements. Study of the processes affecting solutes is an important undertaking, as pollutants may pose a threat to public health when the affected waterbody is used as a water supply or for recreational purposes. Another important issue is the effect of pollutants on the aquatic organisms that inhabit the stream ecosystem.

Naturally occurring solutes are also of interest as they often interact with pollutants, thereby intensifying or diminishing the toxicity of the pollutant. In addition, human activity may affect the concentrations of naturally occurring solutes, leading to the degradation of water quality. A classic example of this is the depressed dissolved oxygen levels that are frequently observed downstream from waste water treatment plants (WWTPs). These low oxygen levels are a direct result of the biochemical oxygen demand exerted by the nutrients contained in the WWTP effluent. Nutrients also play a role in eutrophication, the process wherein abnormally high nutrient concentrations cause excessive plant growth. Anthropogenic causes of eutrophication include failing septic systems, agricultural runoff, and WWTP discharges. A final example is the elevated concentrations of trace elements observed in streams that are acidic due to the effects of acid deposition and acid mine drainage.

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A variety of processes determine the fate and transport of solutes within rivers and streams. To a casual observer, the most obvious processes are those which cause solutes to move downstream and to mix with other constituents in the water column. These *physical processes* are readily apparent to anyone who has ever observed the journey of a fallen leaf as it floats upon the water surface. Closer inspection of the problem indicates that other processes are at work. These additional processes are the chemical and biological reactions that influence solute concentrations. While it is interesting to study individual processes, it is important to consider the complex interaction of the physical, chemical and biological processes. Physical transport characteristics, for example, often determine the residence time of a given solute in the system under study. The residence time effectively determines the time scales over which chemical and biological processes have an effect. The various processes are therefore coupled, such that many complex interactions must be considered within the solute transport problem.

The basic solute transport problem may be formulated in one of two ways. One approach is to state the problem as that of prediction; given the solute concentration at a specific point in time and space, what are the solute concentrations at various locations downstream at some future time? A second approach is to state the problem in a descriptive manner; given a time series of solute concentrations along the stream, what are the dominant processes controlling solute concentrations? Consideration of either question requires a clear definition of the problem. Problem definition begins with a determination of the primary solute of interest. A second task is to define the secondary solutes that interact with the primary solute through chemical and biological processes such as co-precipitation, sorption and oxidation-reduction. The next step is to determine the potential sources of solute mass for the set of solutes under study. Given this information, the dominant processes are elucidated. A final task is to define the environmental forcing functions such as temperature, *p*H and meteorological variables that influence the rates of the dominant processes.

The goal of this chapter is to describe the concepts necessary to solve the problem described above. Many of these concepts are drawn from our research on the hydrology and geochemistry of small mountain streams. This is an appropriate focus as many of the concepts presented are equally applicable to larger rivers and streams. Our discussion also has relevance to larger systems in that small, upland streams may significantly affect the water quality of larger river systems located downstream. Finally, our focus on small streams highlights the scale dependence of the solute transport problem. In the discussion that follows, we are concerned with streams in which flow is predominantly uni-directional. This one-dimensional approach is frequently used for the analysis of solute transport in small streams, and is often applied to larger streams.

This chapter begins with a description of the physical mechanisms that influence solute transport. These physical processes affect both conservative, or inert, solutes, as well as nonconservative, or reactive, solutes that are affected by chemical and biological processes. This discussion is an appropriate starting point as a thorough understanding of physical transport is needed before one may consider the complex interaction between the hydrologic system and the biogeochemical regime. A second topic is the spatial and temporal distribution of the sources that contribute solute mass. This is important topic as spatial and temporal variability affects the manner in which we address the solute transport problem. Traditional analyses of solute transport have focused on point sources of pollution such as outfalls from WWTPs. Many current environmental issues, however, concern distributed sources which are nonpoint in space and/or continuous in time. We conclude the chapter with a brief overview of some basic chemical processes controlling solute concentrations. For simplicity, biological processes are not considered herein.

Within the context of the specific topics described above, we wish to make two important points. First, study of solute transport in streams entails more than a study of the stream itself; a thorough study must consider the relationship of the stream to the surrounding watershed, and the associated hydrologic and geochemical implications. Second, streams are complex ecosystems in which a variety of processes control solute concentrations. Consideration of any one process tells only part of the story, such that the system must be considered as a whole. This holistic view requires explicit consideration of the time-scales over which the various processes influence solute behavior. Finally, we wish to state that our discussion of many of the topics described herein is necessarily brief. More complete descriptions may be found in one of several textbooks on water quality modeling and management [*Fischer et al.*, 1979; *Reckhow and Chapra,* 1983; *Chapra and Reckhow*, 1983; *Tchobanoglous and Schroeder*, 1985; *Thomann and Mueller*, 1987].

Physical Transport Processes

Physical processes play an important role in determining the fate of solutes in surface water environments. For example, consider the release of dye into the center of a free-flowing stream. Upon entering the stream, the dye forms a cloud that moves downstream with the flowing waters. This process, known as *advection*, describes the downstream transport of solute mass at the mean flow velocity. As the dye moves downstream, small-scale mixing processes cause the dye to spread out, or disperse, thereby increasing the volume and decreasing the concentration of the dye-containing water. This spreading process is called *dispersion*.

Dispersion is attributed to both molecular diffusion and velocity variations caused by shear stress. Molecular diffusion occurs due to the random motion of particles, as illustrated in Figure 1. Figure 1a depicts a rectangular tank that is split in half by an impermeable divider. A soluble substance is added to the left half of the tank, while the right half of the tank contains distilled water. At some initial time, t_0, the molecules of the substance are uniformly distributed such that the concentrations at any two locations in the left half of the tank are identical. The remaining panels in the figure show the distribution of molecules after the divider is removed from the tank. Figure 1b shows the tank at an intermediate time ($t > t_0$), when 25 percent of the molecules have entered the right half of the tank. Given sufficient time ($t >> t_0$), the random motion of particles results in a uniform distribution of molecules, as shown in Figure 1c.

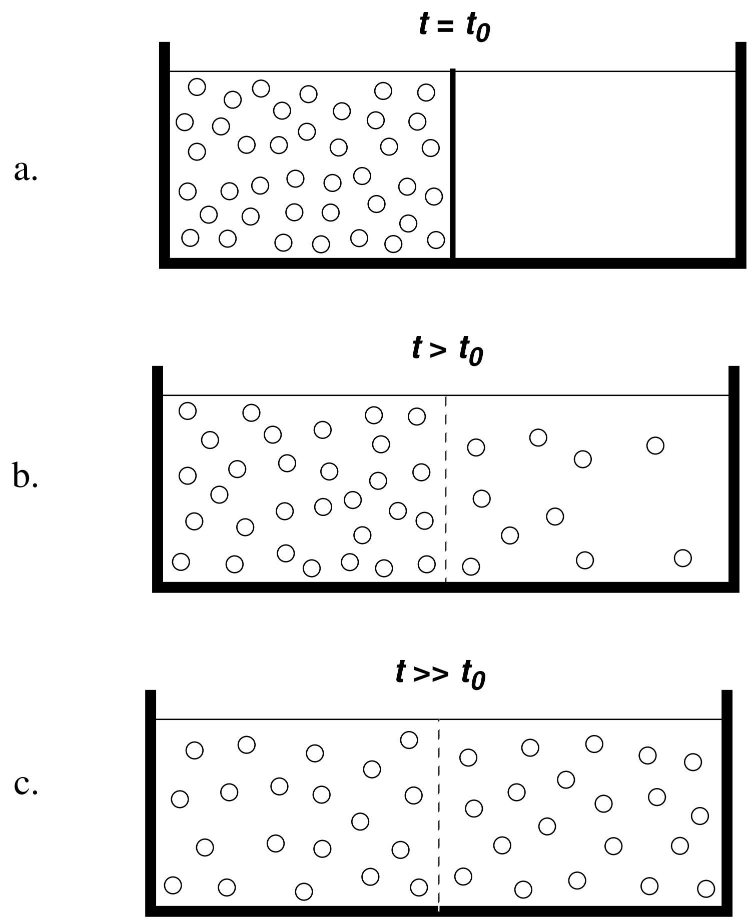


Figure 1: Rectangular tank depicting molecular diffusion. a) At time t_0, impermeable divider separates the left side of the tank, containing molecules of a soluble substance, and the right side of the tank, containing distilled water. b) After the divider is removed, random particle motion causes molecules to make their way into the right side of the tank. c) After a long period of time, random particle motion results in a uniform distribution of molecules throughout the tank.

Molecular diffusion may be a significant mixing process in waters with low flow velocities, such as quiescent lakes and groundwaters. The role of molecular diffusion is often diminished in streams and rivers, however, as velocity variation becomes the dominant mixing mechanism. This mixing arises due to the effects of friction or shear stress on the velocity profile. Figure 2a shows a vertical velocity profile of a typical stream. Due to the rough nature of the streambed, longitudinal velocity is at its minimum near the streambed. Velocity generally increases with distance from the streambed, but may decrease near the water surface due to the effect of wind shear. Velocity also varies in the horizontal direction, as given by the aerial view shown in Figure 2b. In this direction, velocity is at its maximum at the centerline of the stream and decreases as the stream bank is approached. These vertical and horizontal velocity variations cause considerable mixing as particles within the water column travel at different velocities.

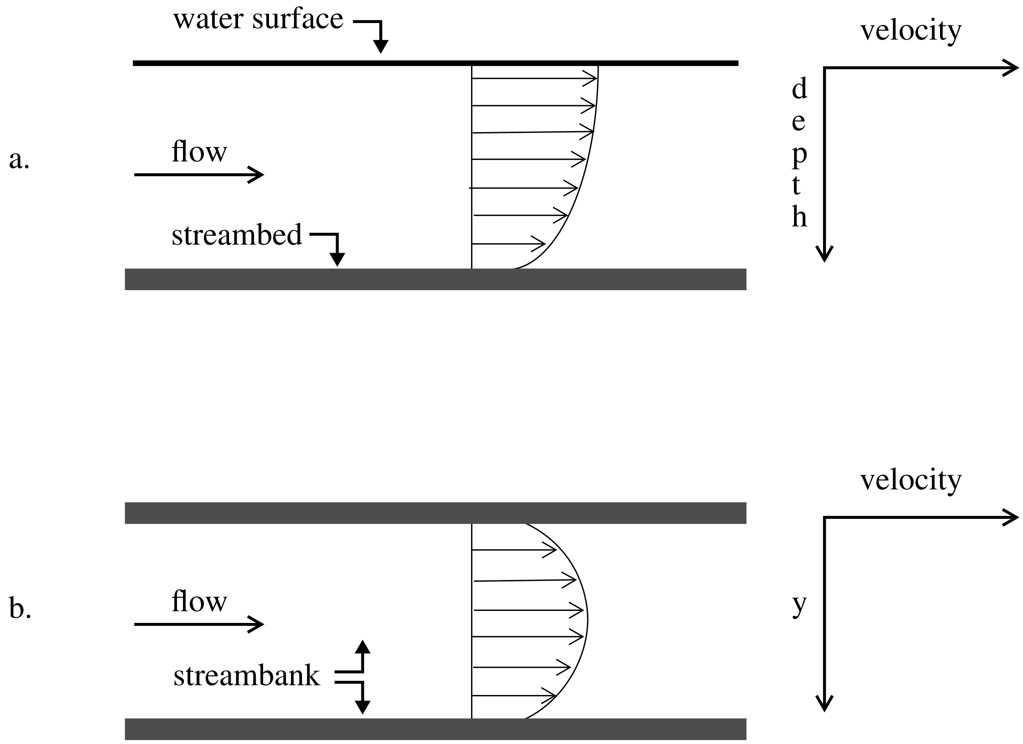


Figure 2: Velocity variations due to shear stress. a) Vertical velocity profile in a stream. b) Horizontal velocity profile in a stream.

The combined effects of advection and dispersion are depicted in Figure 3, where the size and location of our hypothetical dye cloud is given for three scenarios. Figure 3a shows the appearance of the dye to a stationary observer for the case of advection only. After the dye is placed in the stream at time t_0, the location of the dye cloud changes for times greater than t_0, but the volume of the dye cloud remains constant with time. When dispersion is the only transport process considered, as in Figure 3b, the center of the dye cloud remains stationary, but the volume of dye-containing water increases with time. The behavior of the dye in a real stream is most accurately shown in Figure 3c, where both advection and dispersion are considered. For this final scenario, the location of the dye changes due to advection, and the volume of the dye-containing water increases due to dispersion.

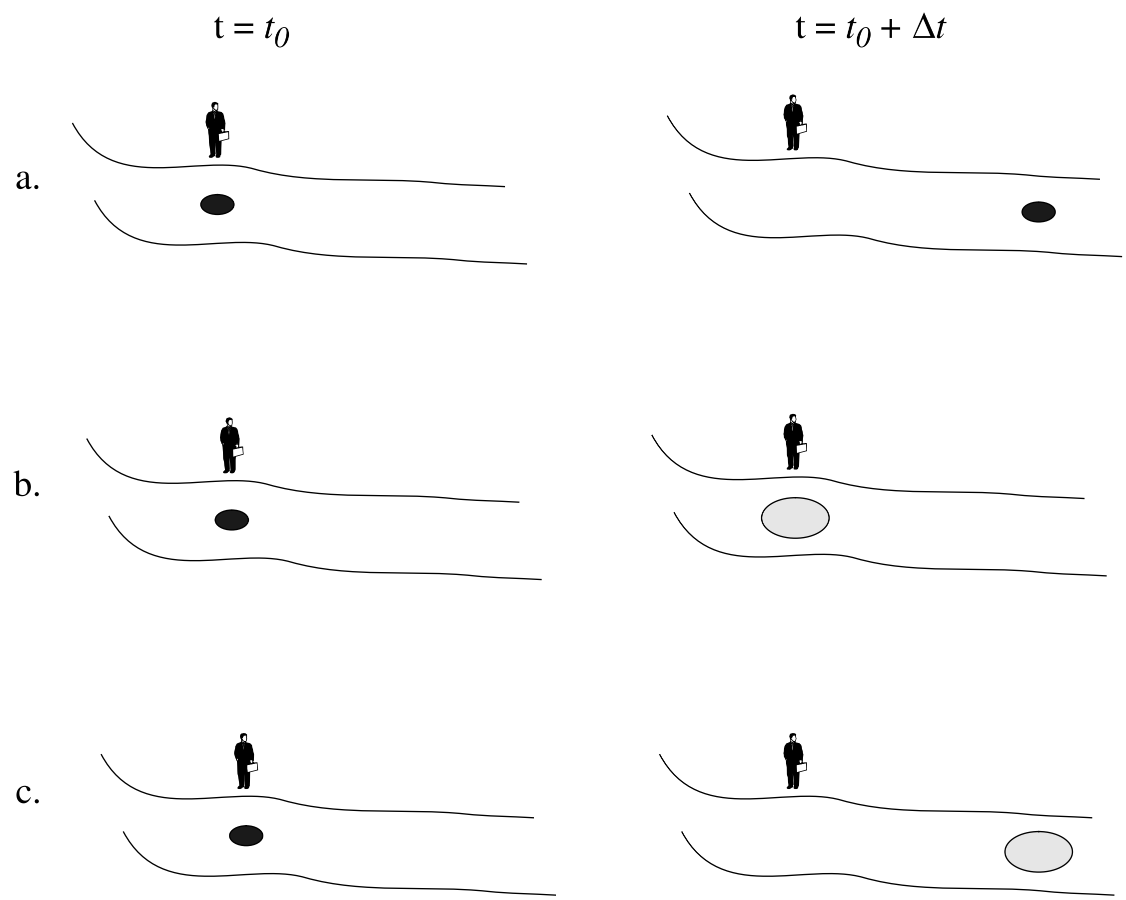


Figure 3: Effects of advection and dispersion on a cloud of dye. a) the case of advection only; the location of the dye cloud changes with time but its volume is constant. b) the case of dispersion only; the center of the dye cloud is stationary but the volume increases. c) combined effect of advection and dispersion; the location and volume of the dye cloud changes with time.

An equation describing the spatial and temporal effects of advection and dispersion on solute concentration is presently developed using a fundamental concept, *conservation of mass*. Conservation of mass simply states that the accumulation of mass in a unit volume of water is equal to the difference between mass entering the volume and mass leaving the volume:

$$Accumulation = Mass\ In - Mass\ Out \tag{1}$$

where each term in the equation is expressed in units of mass per time [M/T][1].

The *mass balance equation* given above is formally developed by considering the fluxes in and out of a *control volume* shown in Figure 4. For simplicity, we assume that our stream is spatially uniform, *i.e.*, the flow, cross-sectional area and mixing properties of the stream do not vary in space. Furthermore, we assume *steady flow*, such that the velocity and volume of water do not change with respect to time. Finally, we consider only inflows and outflows in the x direction, neglecting fluxes across the y and z planes. In doing so we implicitly assume that solute concentrations vary only in the downstream (x) direction and that solute mass is uniformly distributed over the stream's cross-sectional area [*Fischer et al.*, 1979]. Although this uniformity rarely occurs in nature, our one-dimensional approach is reasonable for streams of small to moderate width and depth.

[1]For the remainder of this chapter, physical quantities are described using the fundamental units of mass [M], length [L] and time [T].

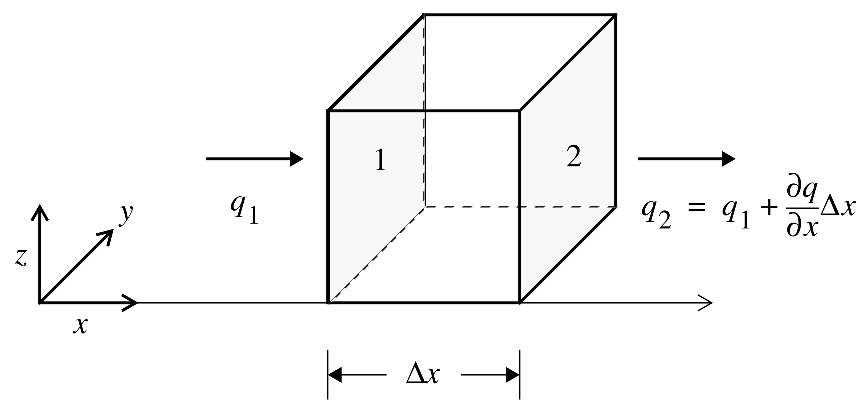


Figure 4: Unit volume of water (control volume) used to develop the conservation of mass equation. A mass balance equation is developed by considering the fluxes into the volume across surface 1 and the fluxes out of the volume across surface 2. Fluxes in the *y* and *z* direction are not considered.

The first term in Equation (1) describes the accumulation of mass or the change in mass with respect to time. Using differential calculus, this is given by:

$$Accumulation = \frac{\Delta m}{\Delta t} = \frac{\partial m}{\partial t} \tag{2}$$

where m is mass and t is time. Noting that mass equals concentration times volume and employing our constant volume assumption yields:

$$Accumulation = V\frac{\partial C}{\partial t} \tag{3}$$

where V is volume [L^3] and C is solute concentration [M/L^3]. The right-hand side of Equation (1) is developed by considering the *flux* of solute mass across surfaces 1 and 2 denoted in Figure 4. The flux, q, is defined as the mass of solute crossing a unit area per unit time. The flux into the control volume is denoted by q_1 and flux out of the control volume is denoted by q_2. Note that q_2 equals the flux coming into the control volume (q_1) plus the change in flux through the control volume:

$$q_2 = q_1 + \frac{\partial q}{\partial x}\Delta x \tag{4}$$

where Δx is the length of the control volume [L].

We now consider the individual fluxes due to advection and dispersion. The advective flux into the control volume (across surface 1) equals the product of the advective velocity, U [L/T], and the solute concentration at surface 1, C_1:

$$Flux\ In_{adv} = q_{1_{adv}} = UC_1 \tag{5}$$

Employing Equation (4), the advective flux out of the control volume (across surface 2) is given by:

$$Flux\ Out_{adv} = q_{2_{adv}} = UC_2 = UC_1 + U\frac{\partial C}{\partial x}\Delta x \tag{6}$$

where C_2 is the solute concentration at surface 2.

Fluxes due to dispersion are developed by considering a fundamental law governing *diffusive* mass transport. *Fick's Law of Diffusion* states that mass flux due to molecular diffusion is proportional to the concentration gradient, $\partial C/\partial x$. By analogy, this law may be used to describe the dispersive mass flux. This flux is given by:

$$q_{disp} = -D_L\frac{\partial C}{\partial x} \tag{7}$$

where D_L is a proportionality constant known as the *longitudinal dispersion coefficient* [L^2/T]. Dispersive flux into and out of the control volume is thus given by:

$$Flux\ In_{disp} = q_{1_{disp}} = -D_L \frac{\partial C}{\partial x}\bigg|_1 \tag{8}$$

$$Flux\ Out_{disp} = q_{2_{disp}} = -D_L \frac{\partial C}{\partial x}\bigg|_2 = -\left[D_L \frac{\partial C}{\partial x}\bigg|_1 + D_L \frac{\partial^2 C}{\partial x^2}\Delta x\right] \tag{9}$$

A differential equation corresponding to Equation (1) is now assembled using the accumulation and flux terms developed above. Equations (3), (5), (6), (8) and (9) are combined to give:

$$\underbrace{V\frac{\partial C}{\partial t}}_{\text{Accumulation}} = \underbrace{\left[AUC_1 - AD_L \frac{\partial C}{\partial x}\bigg|_1\right]}_{\text{Mass In}} - \underbrace{\left[AUC_1 + AU\frac{\partial C}{\partial x}\Delta x - AD_L \frac{\partial C}{\partial x}\bigg|_1 - AD_L \frac{\partial^2 C}{\partial x^2}\Delta x\right]}_{\text{Mass Out}} \tag{10}$$

where A is the stream's *cross-sectional area* [L^2]. Because flux is specified on a per unit area basis, each flux is multiplied by A to obtain the units used in Equation (1) [M/T]. Using the relation $V = A\Delta x$, Equation (10) is simplified to yield:

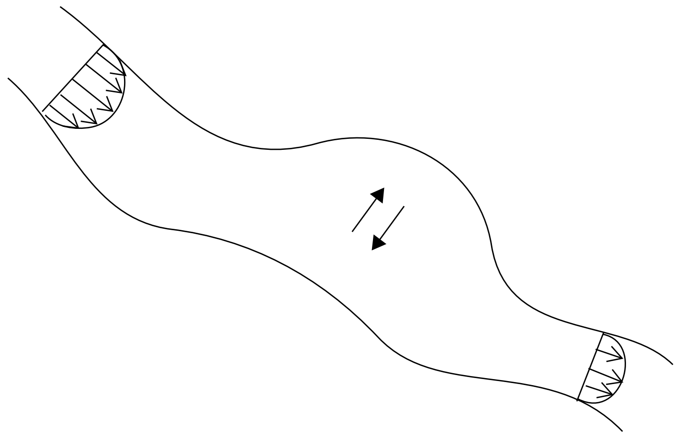
$$\frac{\partial C}{\partial t} = -U\frac{\partial C}{\partial x} + D_L \frac{\partial^2 C}{\partial x^2} \tag{11}$$

This equation is the *Advection-Dispersion Equation* with constant coefficients (*i.e.*, U and D_L are constant in space and time). The advection-dispersion equation describes the spatial and temporal variation in solute concentration, C, subject to the assumptions given previously. An explicit equation for C as a function of space and time is given in the section that follows.

Although advection and dispersion are the dominant physical processes affecting solutes in many surface waters, other physical processes may be of importance for a given water body. For example, many small streams and rivers gain significant amounts of water from *lateral inflows*. As defined here, lateral inflow is any water that is added to the stream due to groundwater inflow, overland flow, interflow or via small springs and seeps. As a result of lateral inflows, the volumetric flowrate of the stream, Q [L^3/T], increases in the downstream direction. It is important to note that these lateral inflows are not only a source of water to the stream, but also a source of solute mass. For a given stream reach, the lateral inflow concentration, C_L, represents the average solute concentration associated with the waters added by lateral inflow. If C_L is less than the instream concentration, C, lateral inflow has the effect of diluting the instream concentration. Conversely, if the lateral inflow concentration exceeds the instream concentration, the lateral inflow waters act to increase the instream concentration. As shown below, terms may be added to the advection-dispersion equation to account for the effects of lateral inflow.

Another physical process of importance in some systems is that of *transient storage* [*Bencala and Walters*, 1983]. Transient storage has been noted in many small streams, where solutes may be temporarily detained in small eddies and stagnant zones of water that are stationary relative to the faster moving waters near the center of the channel. In addition, significant portions of the flow may move through the coarse gravel of the streambed and the porous areas within the stream bank. The travel time for solutes carried through these porous areas may be significantly longer than that for solutes travelling within the water column. These pockets of water and porous areas of the streambed are the two areas contributing to transient storage, as shown in Figure 5.

a.



b.

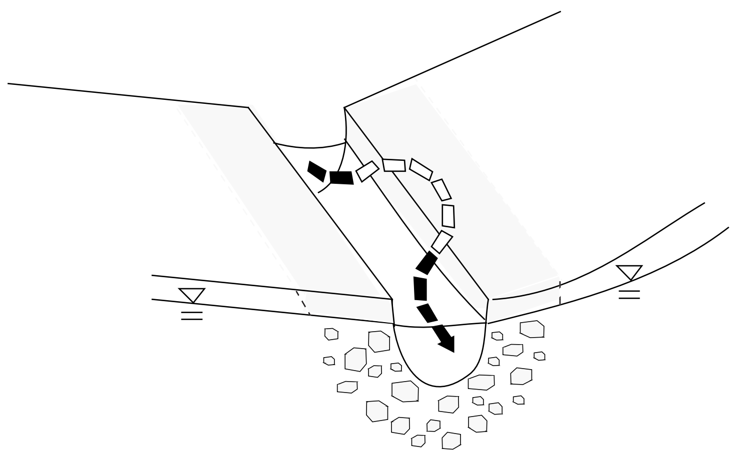


Figure 5: Transient Storage occurs when solutes enter small pockets of slow moving water (a) and when solutes travel through the porous media that makes up the bed and banks of the channel (b).

The effects of transient storage are illustrated by examining data from a tracer experiment shown in Figure 6 [*Broshears et al.* 1993]. In a tracer experiment, a conservative tracer is injected into the stream and samples are taken at various downstream locations. Shortly after the injection begins, the concentration of the injected solute increases at each sampling site (Figure 6a). As the injection continues, the tracer concentration reaches a plateau level that is maintained until the injection is shut off. After the injection ceases, the tracer concentration gradually declines to its pre-injection level.

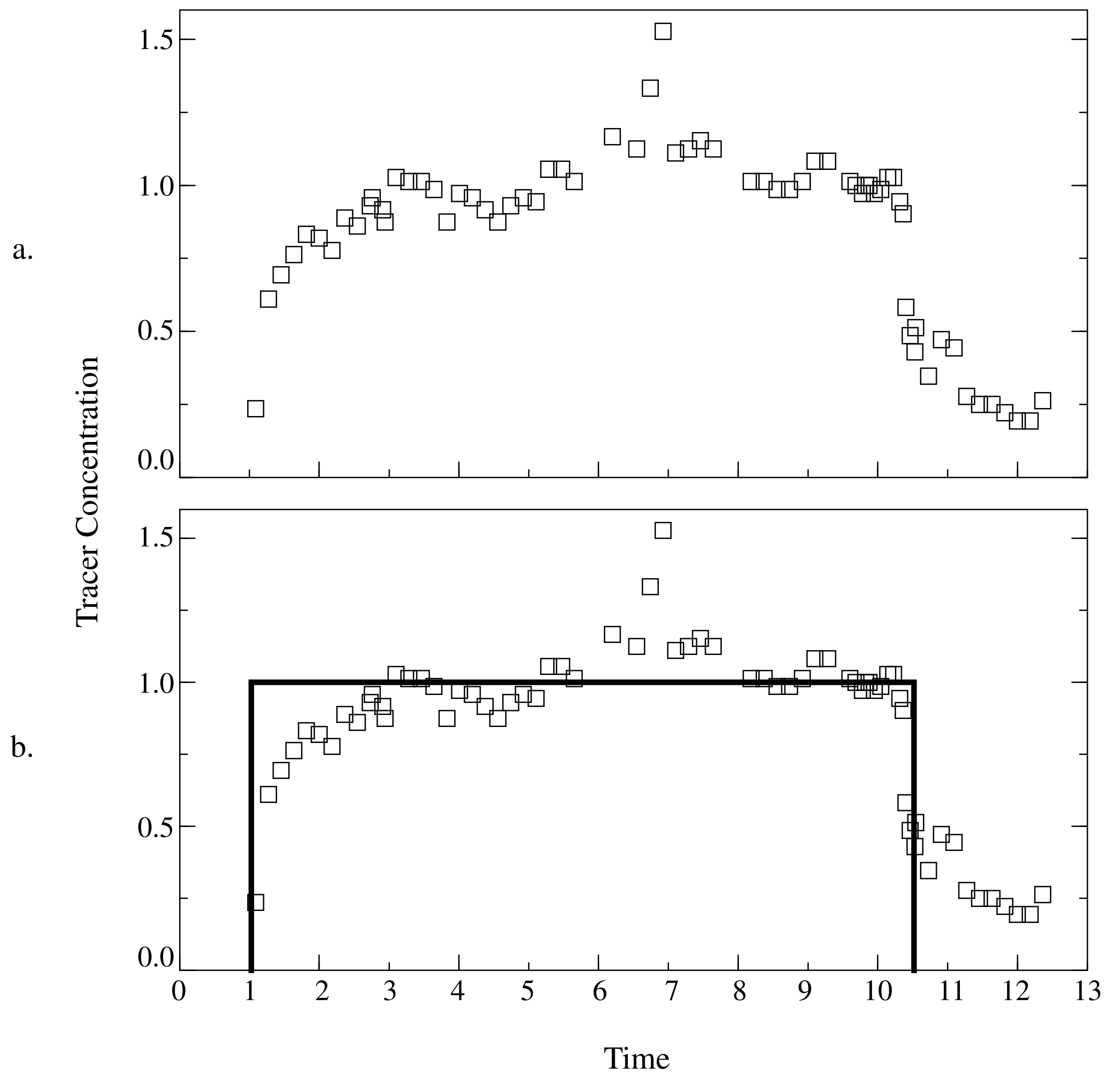


Figure 6: Experimental tracer data illustrating the effect of transient storage. a) tracer concentration at a downstream sampling location. Tracer concentration increases after the injection begins, reaches a plateau and decreases after the injection terminates. b) rectangular pulse showing hypothetical tracer concentration in the absence of dispersion and transient storage. Observed concentrations differ from the hypothetical case due to dispersion and transient storage. (Adapted from *Broshears et al.*, 1993).

In Figure 6b, a rectangular area is superimposed over the tracer data. This rectangular pulse indicates the tracer concentration that would result if tracer mass was transported downstream by advective processes alone. Departures from this hypothetical concentration profile are due to the effects of mixing. Analysis of tracer data using the advection-dispersion equation derived previously accounts for some of the observed mixing through the specification of the longitudinal dispersion coefficient. The general shape of the concentration profile cannot be described by this analysis alone, however, and additional mixing due to transient storage must be considered.

Two characteristic time periods of the observed profile are of interest. The first period relates to the arrival of the tracer pulse. As indicated by the rectangular region, the tracer concentration instantaneously increases to the plateau concentration (1.0) in a purely advective system. The arrival of the tracer pulse is delayed for the real stream, however, as indicated by the gradual increase in tracer concentration. This delayed arrival is due to dispersion and the movement of tracer mass into the transient storage areas. During this initial time period, the transient storage zones act to reduce tracer mass in main channel, as the tracer makes its way into the streambed and the slow moving pockets of water. A second time period of interest corresponds to the cessation of the tracer injection. Given a purely advective system, the tracer concentration drops instantaneously from the plateau concentration to background concentration, as indicated by the right edge of the rectangular region. In the real stream, this decrease is more gradual, as indicated by the concentration tail observed in the data. During this time period, the tracer concentration in the storage zones generally exceeds that in the main channel, and tracer mass bleeds out of the storage zones producing the observed tail. In summary, the transient storage zones act as a sink during the initial stages of the tracer injection and a source of tracer during the latter stages.

To conclude our discussion on physical transport mechanisms, we briefly revisit the advection-dispersion equation given as Equation (11). Our derivation of this equation considers the processes of advection and dispersion, but neglects the effects of lateral inflows and transient storage. In addition, our assumptions result in an equation that is restricted to the case of spatially constant parameters and a steady flow regime. Most of us realize, however, that real streams are not spatially uniform, as the cross-sectional area varies over short distances and structural features such as boulders and tree stumps influence mixing processes. Furthermore, instream flowrates vary in time due to the effects of rainfall, snowmelt, evapotranspiration and the appropriation of water. Fortunately, a derivation similar to that provided above may be used to develop a general transport equation that encompasses the effects of advection, dispersion, lateral inflow and transient storage, while eliminating the restrictions of spatially and temporally constant parameters. This derivation produces:

$$\frac{\partial C}{\partial t} = -U\frac{\partial C}{\partial x} + \frac{1}{A}\frac{\partial}{\partial x}\left(AD_L\frac{\partial C}{\partial x}\right) + \frac{q_L}{A}(C_L - C) + \alpha(C_S - C) \qquad (12)$$

where q_L is the lateral inflow rate per unit length of stream [L^3/T-L] and α is a first order mass-transfer coefficient controlling the rate of exchange between the main channel and the transient storage zone [/T]. Note that Equation (12) also introduces C_S, the average solute concentration in the storage zone [M/L^3]. Assuming waters in the storage zone are immobile relative to waters in the main channel, an equation describing C_S is given by [*Bencala and Walters*, 1983]:

$$\frac{dC_S}{dt} = \alpha\frac{A}{A_S}(C - C_S) \qquad (13)$$

where A_S is the cross-sectional area of the storage zone [L^2].

Sources of Solutes

Up until this point we have been concerned with the physical processes affecting solutes after they enter the stream. In this section we examine the pathways in which solutes enter the surface water environment. In our earlier example, a quantity of dye was added to a small stream or river. This dye was added at a specific point in space, and the addition occurred over a specific time period. Thus the addition of dye has both spatial and temporal components. Specifically, the dye addition represents a *point source* and an *instantaneous* release. As we see in this section, sources of solutes vary in both time and space. If the solutes of interest are environmental contaminants, this variability may be an important factor in determining the ultimate impact of the contaminants on the stream environment.

From a spatial perspective, solutes enter surface waters through *point* and *nonpoint* sources. As the name implies, point sources introduce solutes at well defined locations along the watercourse. Examples of point sources include discharges from municipal wastewater treatment plants and industrial facilities (Figure 7a), and spills that occur due to accidents, when transporters of hazardous materials release contaminants into a waterbody (Figure 7b). From the standpoint of environmental monitoring, point sources are relatively easy to quantify. Mass loading, for example, may be estimated by measuring the flow and solute concentration associated with a plant's effluent (Figure 7a):

$$W = Q_e C_e \tag{14}$$

where W is mass loading rate [M/T], Q_e is the volumetric flowrate for the point source and C_e is the solute concentration in the effluent. Calculations of mass loading rates are often more difficult than Equation (14) suggests, however, as Q_e and C_e frequently vary in time. The mass loading rate may be incorporated into the mass balance equations presented in the foregoing section.

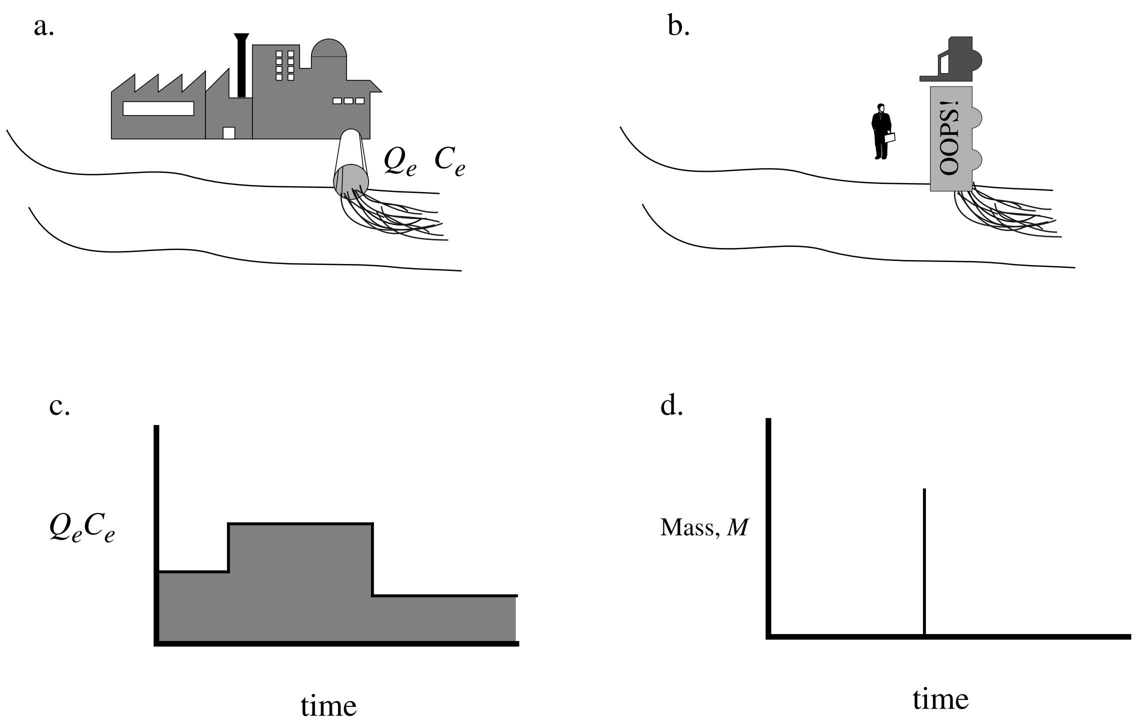


Figure 7: Point sources of solutes. a) Discharges from municipal wastewater treatment plants and industrial facilities. b) Accidental spills from hazardous carriers. c) Point sources such as wastewater treatment plants (Figure 7a) may be continuous sources. d) Point sources such as accidental spills (Figure 7b) may be viewed as instantaneous sources.

Nonpoint sources are sources of solutes that are distributed along the watercourse. These sources are often diffuse, in that mass entering at any one point in space is relatively small, yet the aggregate mass loading rate is significant. An example of a nonpoint source is agricultural runoff that enters a stream as overland flow (Figure 8a). During precipitation events, runoff from cultivated fields may contain pesticide residues and fertilizer, as well as suspended sediments that sorb contaminants. Loading due to this type of nonpoint source is represented by the lateral inflow terms in the general transport equation [q_L and C_L of Equation (12)]. Another example of a nonpoint source is that of acid deposition (Figure 8b). Due to the burning of fossil fuels, rainfall in some areas of the United States is acidic [*Drever*, 1988]. In addition, acidic particulate matter may deposit on the land surface. This loading may impact a watershed, leading to the acidification of surface waters [see Chapter xx].

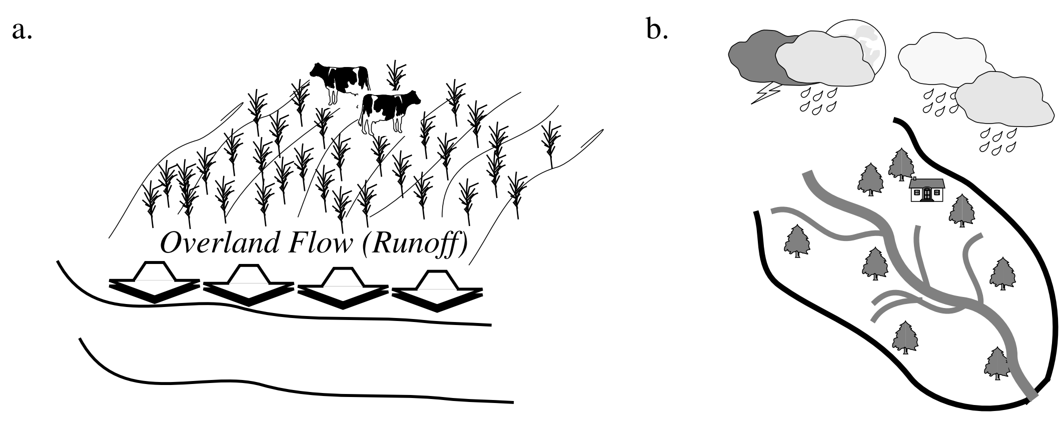


Figure 8: Examples of distributed or nonpoint sources. a) Runoff containing pesticide residues and fertilizers from cultivated lands. b) Acid deposition.

Because they are not associated with a specific point in space, mass loading rates for nonpoint sources are often difficult to quantify. The lateral inflow solute concentration (C_L), for example, may vary dramatically between different sampling locations along the stream [*Bencala and McKnight*, 1987]. For the case of acid deposition, rain gages distributed throughout the watershed may indicate different rates of mass loading. Due to these complications, care must be taken when designing sampling programs to monitor nonpoint sources of pollution.

Solute sources and loading rates also vary with respect to time. Sources may be roughly classified according to their duration. Some sources are *continuous* sources while others may be viewed as being *instantaneous*. Continuous sources introduce solutes to the stream for extended periods of time. An example of a continuous source is the wastewater treatment plant shown in Figure 7a. Although mass loading rates may vary in time (Figure 7c), many of these plants continuously discharge effluent into receiving waters, resulting in a continuous addition of solutes to the stream.

Instantaneous sources add solute mass to the stream over very short time periods. Although truly instantaneous sources do not exist, situations do arise in which solutes are added to the stream over time intervals that are short relative to the time-scales of interest. The addition of dye discussed in the previous section is one example of an instantaneous source. Another example is an accidental spill such as that depicted in Figure 7b, where contaminants enter a stream in a matter of minutes. For the purpose of analysis, this loading can be viewed as the instantaneous addition of mass at a discrete point in time (Figure 7d).

In order to illustrate the significance of temporal variation, we consider the accidental release of a toxic substance into a small stream. Using our knowledge of physical transport mechanisms, we wish to determine the impact of the release on a fish population 500 meters downstream. The stream is fairly uniform throughout the 500 meter reach, having a cross-sectional area (A) of 0.75 meters^2, a volumetric flowrate (Q) of 0.1 meters^3/second, and a longitudinal dispersion coefficient (D_L) of 5 meters^2/second.

Two cases are of interest: a ‘spill scenario’, where the toxic substance is instantaneously released, and the ‘leak scenario’, where the substance continuously enters the stream for a specified period of time. For the spill scenario, we consider the instantaneous release of 0.5 kg of the toxic substance (Figure 9a). For the leak scenario, we assume that the same amount of mass (0.5 kg) is uniformly released over a two hour time period. This continuous release results in an instream concentration of 694 μg/*l* (micrograms/liter) near that site of the release, that may be modeled as a rectangular input (Figure 9b).

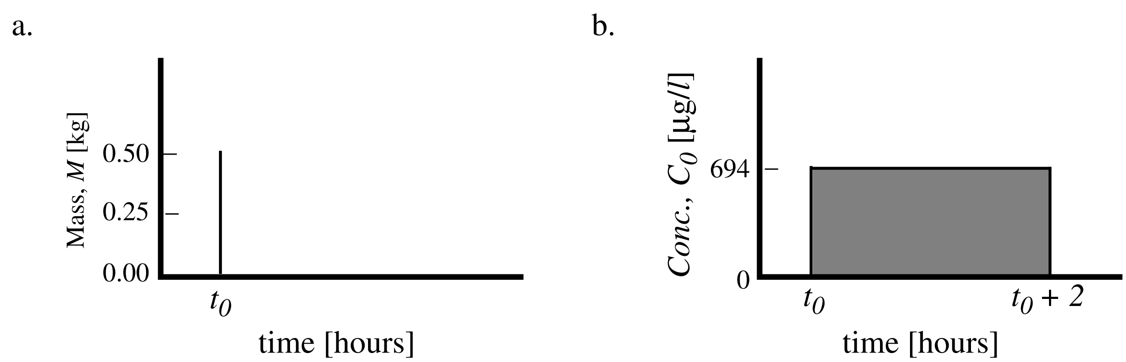


Figure 9: Mass loading scenarios for a hypothetical release. a) Spill scenario is viewed as an instantaneous release of 0.5 kg of mass. b) Leak scenario; mass is released continuously over a two hour period. Concentration in the vicinity of the release is 694 μg/*l*.

These two cases may be analyzed using the advection dispersion equation [Equation (11)]. Using the methods of calculus, *analytical solutions* are developed that provide the predicted solute concentration as a function of time and space. For a spill, the solution to Equation (11) is given by [*Thomann and Mueller*, 1987]:

$$C(x, t) = \frac{M}{2A\sqrt{\pi D_L t}} exp\left[\frac{-(x-Ut)^2}{4D_L t}\right] \tag{15}$$

where M is the mass of the contaminant in the spill and x is distance in the downstream direction. For a continuous rectangular input the solution to Equation (11) is given by [*Fischer et al.,* 1979]:

$$C(x, t) = \frac{C_0}{2}\left[erfc\left(\frac{x-Ut}{2\sqrt{D_L t}}\right) + exp\left(\frac{Ux}{D_L}\right) erfc\left(\frac{x+Ut}{2\sqrt{D_L t}}\right)\right] \qquad \text{for } t < \tau \tag{16}$$

where C_0 is the solute concentration after mixing over the cross-section of the stream, τ is the duration of the continuous input [T] and *erfc* is the complimentary error function. The complimentary error function may be evaluated using tabulated values [*e.g.*, *Eagleson*, 1970; *Freeze and Cherry*, 1979] or numerical techniques [*Press et al.*, 1986]. Note that Equation (16) provides the solution during the duration of the continuous input, *i.e.*, for all $t < \tau$. The principle of superposition may be used to develop the solution for all time periods after the termination of the continuous input (for $t > \tau$). This yields:

$$\begin{aligned} C(x, t) = \frac{C_0}{2}\Bigg[& erfc\left(\frac{x-Ut}{2\sqrt{D_L t}}\right) - erfc\left(\frac{x-U(t-\tau)}{2\sqrt{D_L (t-\tau)}}\right) \\ & + exp\left(\frac{Ux}{D_L}\right)\left\{erfc\left(\frac{x+Ut}{2\sqrt{D_L t}}\right) - erfc\left(\frac{x+U(t-\tau)}{2\sqrt{D_L (t-\tau)}}\right)\right\}\Bigg] \qquad \text{for } t > \tau \end{aligned} \tag{17}$$

These solutions may be applied to our problem to determine the effects of advection and dispersion on solute concentration. Note that these equations do not consider any reactions the substance may undergo after entering the stream. As such, we are considering the worst case scenario, in which the toxic substance is transported conservatively and not allowed to degrade. This solution therefore provides an upper bound on the solute concentrations that are likely to be realized within the stream.

The results of our analysis are shown in Figure 10. The solute concentrations at 500 meters for the instantaneous [Equation (15)] and continuous [Equations (16) and (17)] cases are given in Figure 10a. Two features of the concentration profiles illustrate the marked effect of the time component on solute concentrations and the corresponding implications for our fish population. First, the peak solute concentration for the instantaneous release is approximately double that of the peak for the continuous release (1.4 versus 0.7 mg/*l*). This difference may be important if the concentration at which fish are adversely impacted lies between 1.4 and 0.7 mg/*l*. Second, the duration of elevated toxicant concentrations is longer for the case of the continuous release. Fish are exposed to concentrations exceeding 0.3 mg/*l* for almost twice as long for the continuous release scenario. The relative impact of the release under the two different loading scenarios is therefore dependent on the acute and chronic toxicities of the particular substance for the fish species of interest.

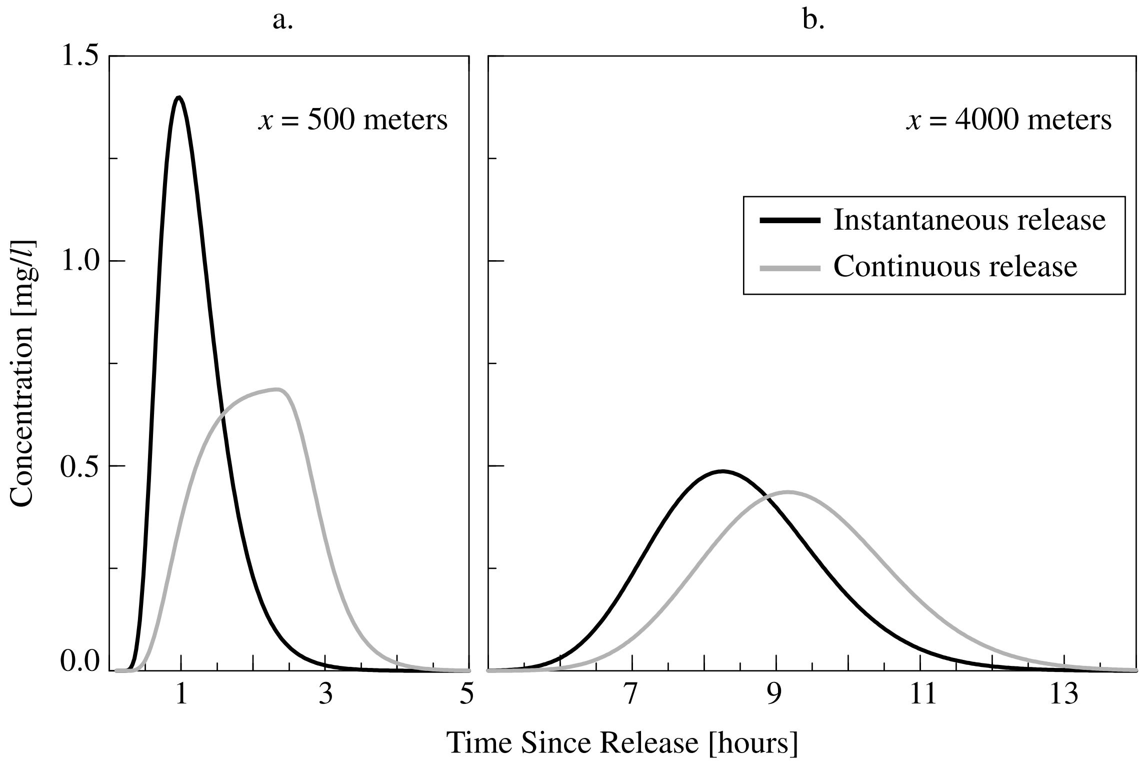


Figure 10: Predicted solute concentrations at two downstream sampling sites. a) At 500 meters, the peak concentration for the instantaneous release is approximately double that of the peak for the continuous release. The duration of exposure is longer for the continuous release. b) At 4000 meters, there is little difference between the concentration profiles for the instantaneous and continuous releases.

Due to the effects of dispersion, the differences attributable to the duration of the release diminish in the downstream direction. This is shown in Figure 10b, where solute concentrations are given for a site 4000 meters downstream. At this location, peak concentrations and exposure durations are approximately equal for the instantaneous and continuous release scenarios.

This example illustrates the effects of source variability and physical processes on the fate of solutes in the stream environment. In the analysis above, we have assumed conservative conditions, such that only the physical processes of advection and dispersion are considered. In many situations, however, the concentration of a released solute may decrease due to sorption, oxidation/reduction, volatilization, hydrolysis, biodegradation and other biochemical processes. These processes are the topic of the following section.

Geochemical Processes

Thus far we have focussed our discussion on the strictly physical processes that affect solute transport. Although physical processes play a large role in determining the fate of solutes, chemical and biological processes may be equally important. In this section we turn our attention to some of the basic geochemical reactions affecting solutes in natural waters. Biological processes are not considered herein.

To illustrate the importance of geochemical reactions, consider the fate of a dissolved chemical species. Dissolved species may take part in both *homogeneous* and *heterogeneous* chemical reactions. Homogeneous reactions are those reactions in which dissolved species interact with other dissolved species. These reactions are homogenous as they involve two or more species of the same phase, *i.e.*, all the species involved in the reaction are in dissolved form. Examples of homogeneous reactions include acid-base, complexation and hydrolysis reactions.

A dissolved species may also take part in heterogenous reactions. In contrast to homogenous reactions, heterogenous reactions involve species from more than one phase. In a heterogenous reaction, a dissolved phase species interacts with gas or solid phase species. Dissolved oxygen concentrations, for example, may be controlled by the oxygen-containing atmosphere overlying the surface water. If dissolved oxygen concentrations are *undersaturated* relative to the gas phase, oxygen will diffuse across the air/water interface and dissolved oxygen concentrations will increase. Conversely, if dissolved oxygen concentrations are *oversaturated*, oxygen will be lost to the atmosphere and dissolved oxygen concentrations will decrease. This process is known as *degassing*. Other examples of heterogenous reactions include solid-phase reactions such as precipitation/dissolution and sorption.

In addition to the reactions noted above, solute uptake and transformation by aquatic organisms is also of importance. Thus we see that there are a variety of processes that may potentially affect the concentration of a given solute. The importance of any particular process is highly dependent on the solute of interest. Interaction with the atmosphere, for example, is often an important process controlling dissolved oxygen concentrations, whereas it is a relatively unimportant process for trace metals. Given this solute-dependence, it is necessary to limit the scope of our discussion to a particular class of solutes. The discussion that follows is therefore based on our experience with inorganic solutes (*e.g.*, salts and trace metals). Organic solutes, including naturally occurring dissolved organic carbon, petroleum-based hydrocarbons, and pesticides, are not explicitly considered. Note, however, that many of the processes and concepts discussed below pertain to organic as well as inorganic constituents. Many excellent reviews of the processes specific to organic solutes may be found in the organic chemistry and groundwater contaminant transport literature [*Lyman et al.*, 1982; *Moore and Ramamoorthy*, 1984; *Princeton University Water Resources Program,* 1984*; Thurman*, 1985; *Devinny et al.*, 1990]. An interesting framework for the analysis of organic fate and transport in surface waters is presented by *Chapra* [1991].

With these points in mind, we now consider some basic geochemical processes. We begin with a discussion of the rates at which reactions occur and two fundamental paradigms for classifying reactions. This is followed by a brief discussion of two reaction classes: precipitation/dissolution and sorption/desorption. The section concludes with a discussion of the role of *p*H and the coupling between hydrologic and geochemical processes. Discussion of each of these topics is necessarily limited. For additional information, the reader is referred to one of several texts on aquatic chemistry [*Snoeyink and Jenkins*, 1980; *Stumm and Morgan*, 1981; *Drever*, 1988; *Pankow*, 1991; *Morel and Hering*, 1993].

Rates of Reaction. Geochemical reactions in natural waters may be studied using one of two fundamental approaches. Selection of the appropriate approach for a given problem is often based on the rates at which the relevant reactions occur, relative to the time scale of interest. If reaction rates are 'slow' relative to the study time scale, a *kinetic* approach is employed, wherein the dynamics of the system are studied. If reaction rates are relatively 'fast', an *equilibrium* approach is implemented to determine the *steady-state* composition of the waters. As explained below, other factors, such as data availability, play a role in determining the appropriate approach.

All geochemical reactions require some finite amount of time, τ_c, to reach completion. The required amount of time is dependent on the rate of reaction, r, such that τ_c and r are inversely related (*i.e.*, if the magnitude of r is small, the reaction proceeds slowly and τ_c is large). A kinetic approach is often implemented when τ_c exceeds the time period of observation, τ_o. For example, τ_c for many biologically-mediated oxidation/reduction reactions is on the order of days to years. If our interest is in the state of the system over the course of a day, a kinetic approach is needed to describe system dynamics, *i.e.*, how the concentrations of the chemical species change over time. In this case, differential equations may be written to describe the temporal variation in species concentrations and kinetic rate constants (r) may be empirically determined. The equations may then be solved to yield the species concentrations over time. Examples of the kinetic approach are given by *Morel and Hering* [1993].

Although the kinetic approach is a useful paradigm for studying dynamic systems, it is not well-suited from many practical geochemical problems. As noted by *Drever* [1988], our knowledge of the kinetics governing many geochemical reactions is incomplete. As a result, kinetic rate information is unavailable for many reactions. In addition, some reactions (*e.g.*, acid-base and complexation reactions) occur at very high rates, such that a study of kinetics is not relevant to the time scales of natural systems. Finally, our observational time period may exceed the time required for the reactions to reach completion ($\tau_o > \tau_c$).

For these reasons, an alternative approach is frequently used to study the system under conditions of chemical equilibrium. The *chemical equilibrium* approach differs from the kinetic approach in that the *steady-state* or equilibrium condition of the system is of interest, rather than the state of the system over time. Consider a reversible chemical reaction in which species A reacts with species B to form species C and D:

$$aA + bB \underset{r_b}{\overset{r_f}{\rightleftarrows}} cC + dD \tag{18}$$

where r_f is the forward rate of reaction, r_b is the backwards rate of reaction, and a, b, c and d are the number of moles of species A, B, C, and D, respectively. Application of the equilibrium approach to this hypothetical reaction is depicted in Figure 11. For this reaction, the chemical equilibrium problem may be stated as follows: "Given an initial state where 'a' moles of A and 'b' moles of B are added to a chemical system, what are the species concentrations (A, B, C and D) at equilibrium?". Here equilibrium is defined as the state of the system at steady-state (as $t \longrightarrow \infty$), given constant environmental conditions such as temperature and pressure.

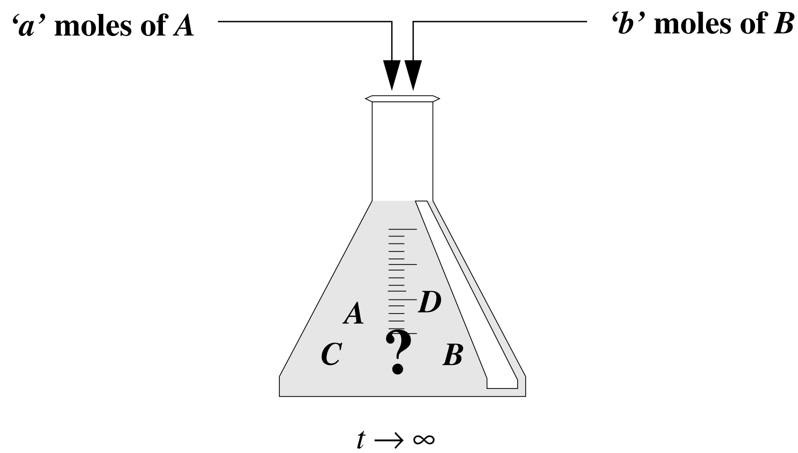


Figure 11: Hypothetical chemical equilibrium problem. If '*a*' moles of *A* and 'b' moles of *B* are added at an initial time, what are the species concentrations (*A*, *B*, *C* and *D*) as $t \rightarrow \infty$?

At equilibrium, the forward rate of reaction equals the backwards rate of reaction and thermodynamic principles may be used to formulate *mass action equations*. The mass action equation corresponding to Equation (18) is given by:

$$\frac{\{C\}^c \{D\}^d}{\{A\}^a \{B\}^b} = \frac{k_f}{k_b} = K_{eq} \tag{19}$$

where k_f is the rate constant for the forward reaction, k_b is the rate constant for the backward reaction, K_{eq} is the equilibrium constant for the overall reaction, and the bracketed (*i.e.*, { }) quantities denote chemical activities. Chemical activities may be considered 'effective concentrations' and are related to observed concentrations using *activity coefficients* [Drever, 1988]. The equilibrium constant therefore defines the concentration ratio of the four species at equilibrium. Mass action equations may be written for all the reactions of interest. These equations are combined with mass balance equations and the resultant system of equations is solved for the equilibrium species concentrations.

Although natural systems are never truly in a state of equilibrium, the equilibrium approach is appropriate for many practical geochemistry problems. As noted above, many reactions occur at very high rates such that the assumption of equilibrium is warranted. For those reactions occurring at slower rates, the equilibrium approach provides valuable insight into system behavior. Equilibrium calculations may be compared with observed species concentrations to determine the degree of disequilibrium. As shown below, these comparisons allow us to determine the direction in which reactions are proceeding.

Precipitation/Dissolution. For inorganic solutes, one of the more dominant chemical reactions is that of precipitation/dissolution. Within a watershed, soil and rock formations near the land surface are subject to weathering reactions that are a source of solutes to surface waters. Limestone deposits, for example, react with water molecules to release both calcium and carbonate. Metallic ores are also subject to weathering reactions and are a source of trace metals such as iron, aluminum and zinc. These trace metals undergo hydrolysis reactions with water to form hydrous metal oxides. Examples of hydrous metal oxides include *ferrihydrite,* $Fe(OH)_3$, and *gibbsite*, $Al(OH)_3$.

In order to illustrate the process of precipitation/dissolution, we consider ferrihydrite, a solid phase that often found on the bed of acidic mountain streams [*McKnight and Bencala*, 1989; *Kimball et al.*, 1992]. Ferrihydrite forms when free ferric iron, Fe^{3+}, combines with hydroxide, OH^-:

$$Fe^{3+} + 3OH^- \Leftrightarrow Fe(OH)_3(s) \tag{20}$$

At equilibrium, this reaction is represented using a mass action equation:

$$\{Fe^{3+}\}\{OH^-\}^3 = K_{sp} \tag{21}$$

where K_{sp} is the *solubility product* for $Fe(OH)_3$ *(s)*. Note that the solubility product is simply an equilibrium constant (K_{eq}, Equation (19)) describing the formation of a solid phase. Recall from our previous discussion that chemical activity is related chemical concentration using activity coefficients. Equation (21) therefore gives the concentrations of the dissolved species, Fe^{3+} and OH^-, that may be in equilibrium with the ferrihydrite solid phase. If the product of the Fe^{3+} and OH^- activities exceeds K_{sp}, the solution is said to be oversaturated and *precipitation* of ferrihydrite from the water column may occur. Conversely, if the product is less than K_{sp}, the solution is undersaturated. If a source of ferrihydrite is present (such as ferrihydrite coating the streambed), undersaturated conditions may result in the *dissolution* of ferrihydrite.

The degree of over or under saturation is quantified by calculating the *saturation index* (SI), a simple function of the *ion activity product* (*IAP*) and the solubility product. The ion activity product is given by:

$$\{Fe^{3+}\}\{OH^-\}^3 = IAP \tag{22}$$

where the product on the left-hand side of Equation (22) refers to ambient conditions and the product on the left-hand side of Equation (21) reflects equilibrium conditions. As such, the ion activity product reflects the current state of the system and the solubility product represents the theoretical equilibrium state. The saturation index is given by:

$$SI = \log\left(\frac{IAP}{K_{sp}}\right) \tag{23}$$

Interpretation of the saturation index is depicted in Figure 12. If the ambient water concentrations (the *IAP*), exceed the equilibrium concentrations (the K_{sp}), the saturation index is positive, indicating oversaturation. Given oversaturated conditions, the reaction given by Equation (20) will tend to proceed to the right. Similarly, if the aqueous concentrations are less than those predicted at equilibrium, the saturation index is negative and the solution is undersaturated. Under these conditions, the reaction given by Equation (20) will tend to the left. Finally, a saturation index of zero indicates that the aqueous solution is in equilibrium with the solid-phase, and the forward and backward reactions given in Equation (20) are in equilibrium.

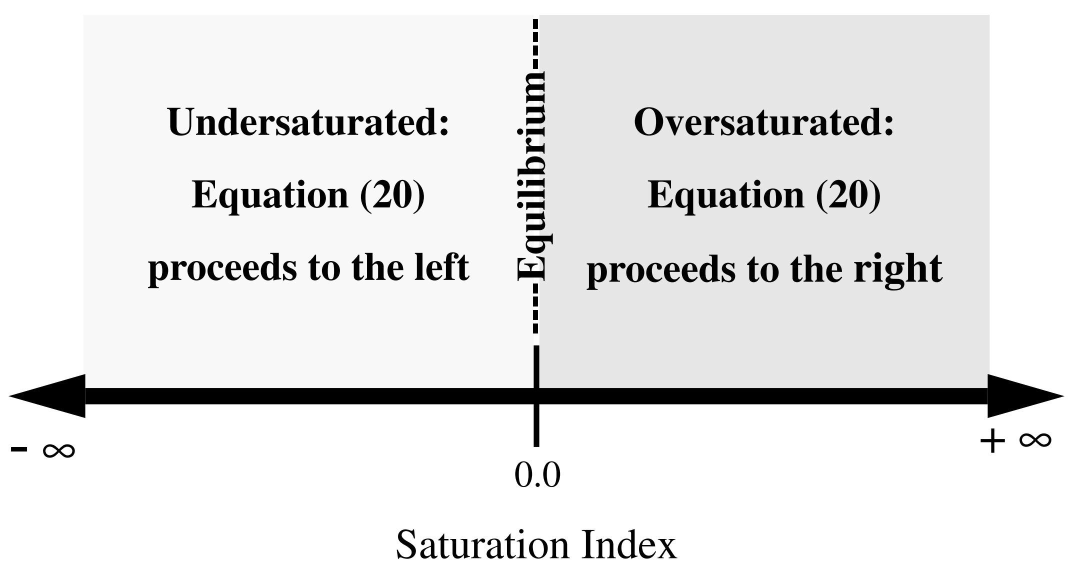


Figure 12: Interpretation of the Saturation Index (SI). The solution may be undersaturated (SI < 0), oversaturated (SI > 0), or at equilibrium (SI = 0), with respect to the controlling solid.

Sorption/Desorption. Another important process controlling the concentrations of solutes in natural waters is that of *sorption*. Sorption may be generally defined as the process in which a dissolved species becomes associated with a solid surface. A dissolved species taking part in a sorption reaction is known as a *sorbate*, and the solid species or sorbing phase is known as the *sorbent*. When the dissolved species interpenetrates the sorbent, the process is termed *absorption*, whereas *adsorption* is used to describe the interaction of the dissolved species with the surface or interface of the sorbent [*Weber et al.*, 1991].

Several physico-chemical mechanisms may be responsible for the sorption process. For example, a dissolved species may form a site specific complex with a sorbent phase. The formation of a chemical complex results in the previously dissolved species being strongly bound to the sorbent. Another potential mechanism is the *electrostatic attraction* that occurs between molecules of opposite charge. Some solid species, such as clays, have a net negative charge that attracts positively-charged metal species. A final mechanism is that of *hydrophobic binding*, wherein nonpolar molecules with a low solubility have an affinity for the solid phase. The specific mechanism responsible for sorption phenomena observed in a given system is a function of both the type of sorbate and the type of sorbent, and in many instances more than one mechanism is at work.

Within natural waters, solutes may sorb to both inorganic and organic sorbents. Inorganic sorbents include alumino-silicates (e.g., red clays), hydrous oxides of aluminum, iron and manganese, and carbonates [*Morel and Hering*, 1993]. Organic sorbents include matter from dead or living organisms and natural organic matter (NOM) that may coat the surface of other solids. In addition to the distinction between inorganic and organic sorbents it is important to note the location of the sorbing phase. Sorption may occur within the water column as dissolved species interact with suspended particles. Sorption may also occur directly on the streambed where the solid phase is abundant. In this latter case, sorption removes solute mass from the water column and the dissolved species is no longer subject to hydrologic transport.

Sorption may have a significant effect on dissolved inorganic species within the water column. As noted by *Morel and Hering* [1993], trace elements such as zinc and copper are known to sorb to hydrous ferric oxides (*e.g.*, ferrihydrite). Sorption onto hydrous oxides may be facilitated by the presence of NOM coatings on the oxide surfaces that impart a negative charge to the sorbent. Other examples of sorption in natural waters include the research of *Bencala et al.* [1983] in which the sorption of strontium and potassium was observed, and the work of *Kuwabara et al.* [1984] wherein copper was found to sorb to the bed of a small stream.

Analysis of sorption reactions is often in the form of *sorption isotherms*. Sorption isotherms are mathematical expressions that relate the mass of solute sorbed to the dissolved solute concentration, for a chemical system at equilibrium. A common approach is to employ the *Freundlich isotherm*:

$$S_e = K_f C_e^n \tag{24}$$

where S_e is the mass of solute sorbed per mass of sorbent [M/M], C_e is the dissolved solute concentration [M/L^3], K_f is the Freundlich isotherm constant [$(L^3/M)^n$], and n is a dimensionless exponent. Note that S_e and C_e are measured when the aqueous system is in equilibrium, *i.e.*, when the rates of sorption and desorption are equal. The logarithmic form of Equation (24) is given by:

$$\log(S_e) = \log(K_f) + n \log(C_e) \tag{25}$$

The two model parameters, K_f and n, represent the sorption capacity and sorption intensity, respectively [*Weber et al.*, 1991]. Parameter estimates are obtained through the analysis of experimental data using Equation (25). In a typical experiment, a known quantity of the sorbent phase and solute are added to a completely mixed batch reactor [*Tchobanoglous and Schroeder*, 1985]. After a sufficient amount of time has passed for the reactions to reach equilibrium, measurements of S_e and C_e are obtained. The experiment is repeated a number of times over a range of initial conditions to yield a set of S_e-C_e pairs that may be graphed on a log-log plot. If the sorption process under study adheres to the Freundlich model, plotted values will form a straight line with slope n and intercept $\log(K_f)$ [Equation (25)]. Given the model parameters, Equation (24) provides a means of calculating the mass of solute sorbed at equilibrium.

For the special case of n=1, Equation (24) reduces to the linear form of the Freundlich equation:

$$S_e = K_d C_e \tag{26}$$

where K_d is known as the *distribution coefficient* [L^3/M]. The distribution coefficient is a physically meaningful parameter as it is a simple ratio of the amount sorbed (S_e) to the amount in the dissolved phase (C_e), at equilibrium. In addition to the Freundlich isotherm, other formulations are possible, such as the Langmuir isotherm.

Although isotherms provide a descriptive framework for the analysis of sorption process, recent research has focused on developing sorption models that are more strongly based in theory. An example of this research is the development of *surface complexation models* [*Dzombak and Morel*, 1990] that consider both the chemical reactions between solutes and functional surface groups (chemical bonding) and electrostatic interactions. Additional details on sorption isotherms and surface complexation modeling are provided by *Morel and Hering* [1993].

***p*H, the Master Variable.** The *p*H of a solution is defined as the negative logarithm of the hydrogen ion activity [$p\mathrm{H} = -\log(\{H^+\})$]. All of the geochemical reactions discussed above are affected by *p*H. In order to illustrate the effect of solution *p*H on reaction chemistry, we now present some experimental data from the Snake River, a naturally acidic stream located in the Rocky Mountains of Colorado. Surface waters become acidic when additions of acid exceed the buffering capacity of the carbonate system. Anthropogenic sources of acidity include acid deposition and acid mine drainage. In addition, some sources of acidity arise naturally due to the oxidation of sulfide bearing ores.

Acidic waters are of concern as their low *p*H increases the solubility and mobility of trace metals. As described by *McKnight and Bencala* [1989], a *p*H modification experiment was conducted on the Snake River to assess the affect of *p*H on trace metal mobility. The experiment involved the injection of a strong acid to temporarily lower the *p*H of the stream. Figure 13a depicts the changes in *p*H in response to the acid injection. At an observation point located 628 meters downstream from the injection, instream *p*H values decreased from approximately 4.2 to 3.2. After 3 hours, the injection was terminated, and instream *p*H values returned to 4.2.

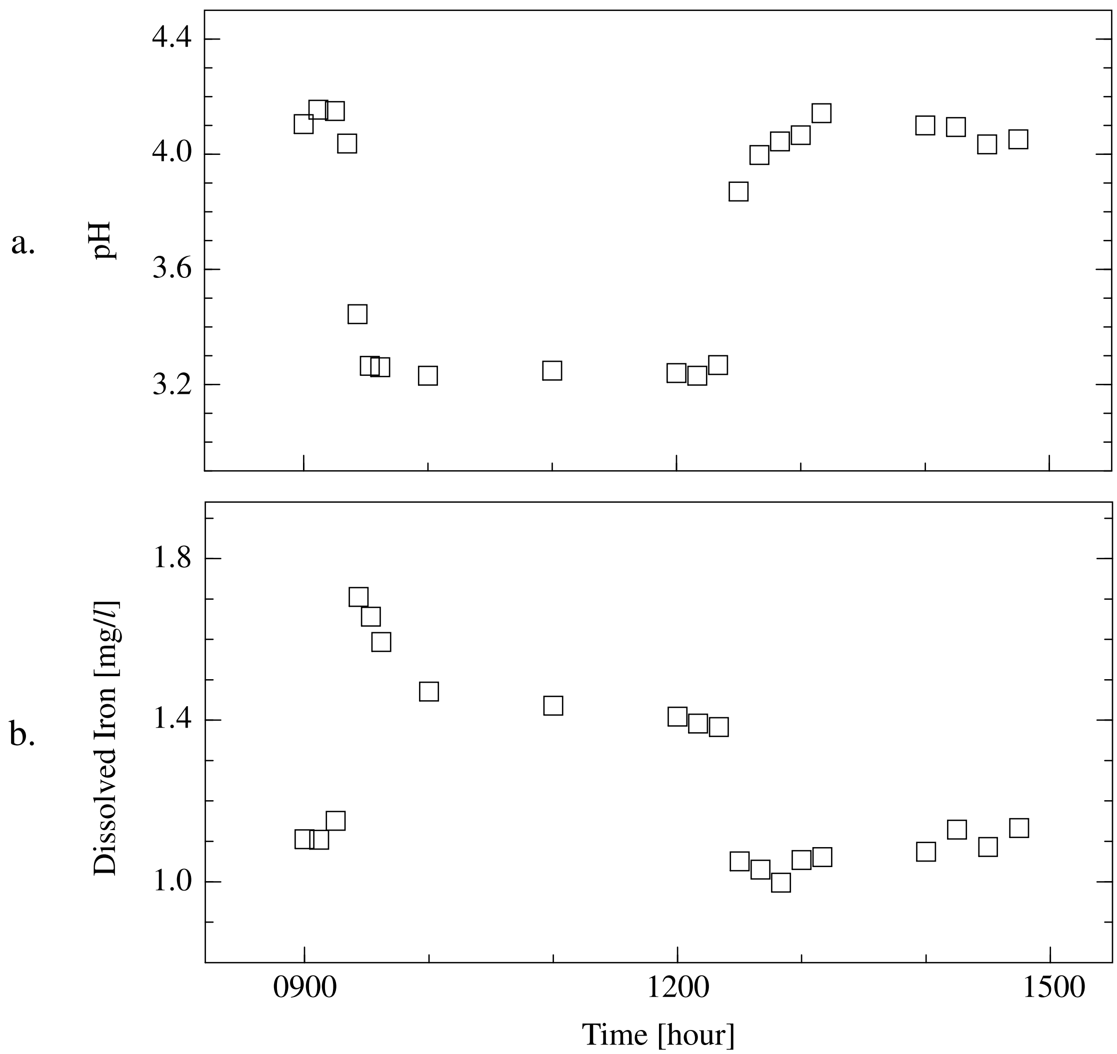


Figure 13: *p*H modification experiment on the Snake River. a) *p*H of the stream was temporarily lowered from 4.2 to 3.2. b) dissolved iron concentrations increased in response to the depression in *p*H.

The effect of the *p*H decrease on dissolved iron concentrations is shown in Figure 13b. As shown in the figure, iron concentrations increased dramatically as the *p*H decreased. Much of this increase is attributable to the dissolution of hydrous iron oxides that coat the streambed. This increase in iron is to be expected in light of the mass action equation governing ferrihydrite precipitation/dissolution [Equation (20)]. In this equation, free ferric iron (Fe^{3+}) activities are related to hydroxide (OH^-) activities to the third power. As a result, small changes in *p*H cause relatively large changes in dissolved ferric iron[2].

The above example illustrates the effect of *p*H on the process of precipitation/dissolution. Many other reactions, including sorption/desorption and oxidation/reduction, are dependent on solution *p*H. Examples of the effect of *p*H on sorption are provided by *Morel and Hering* [1993]. Due to the importance of *p*H, it is often referred to as 'the master variable'.

[2] *p*H is related to the hydroxide activity through the mass action equation describing the dissociation of water: $\{H^+\}\{OH^-\} = K_w$, where K_w is an equilibrium constant.

Coupling of Hydrologic and Geochemical Processes

Thus far we have discussed physical transport mechanisms and geochemical reactions as separate processes. In natural systems, however, these processes are closely coupled. Geochemical reactions determine the distribution of solute mass amongst dissolved, solid and gas phases and thereby affect the amount of mass available for physical transport. Physical transport mechanisms, meanwhile, affect the location of solute mass such that a given parcel of water is subjected to various geochemical regimes as it moves downstream. In this section we examine the coupling of the various processes through several examples.

The coupling between transport and chemistry may be illustrated by revisiting our conceptual classification of geochemistry based on homogenous and heterogenous reactions. This distinction between reaction types becomes important when considered within the context of physical transport. To begin, we divide the heterogenous reactions into three subclasses. Heterogenous I reactions are those reactions in which a dissolved species interacts with a mobile solid species. Examples of Heterogenous I reactions include the formation of a precipitate in the water column due to oversaturated conditions, and the sorption of a dissolved species onto a particulate solid within the water column. Heterogenous II reactions are those in which a dissolved species interacts with a stationary solid species. An example of a Heterogenous II reaction is the sorption of a dissolved species onto a stationary solid such as particles coating the streambed or debris in the channel. Finally, Heterogeneous III reactions are those in which a dissolved species interacts with a gas phase, such as the degassing of dissolved oxygen to the atmosphere.

The effect of the various reaction types on physical transport is depicted as a continuum in Figure 14. At one extreme of the spectrum, geochemical reactions do not affect the amount of mass that is subject to physical transport. Such is the case for homogenous reactions in which dissolved species interact with other dissolved species. In this case, all of the reactants remain in the water column and the net amount of mass subject to transport does not change as a result of the reaction. At the other extreme, geochemical reactions result in a complete loss of mass such that all of the mass involved in the reaction is no longer transported downstream. Heterogenous II and Heterogenous III reactions fall at this end of the spectrum. For Heterogenous II reactions, mass involved in the reaction is deposited on stationary surfaces and is no longer transported. Likewise, Heterogeneous III reactions involve degassing; mass that leaves the stream via the air/water interface is no longer affected by the flowing waters.

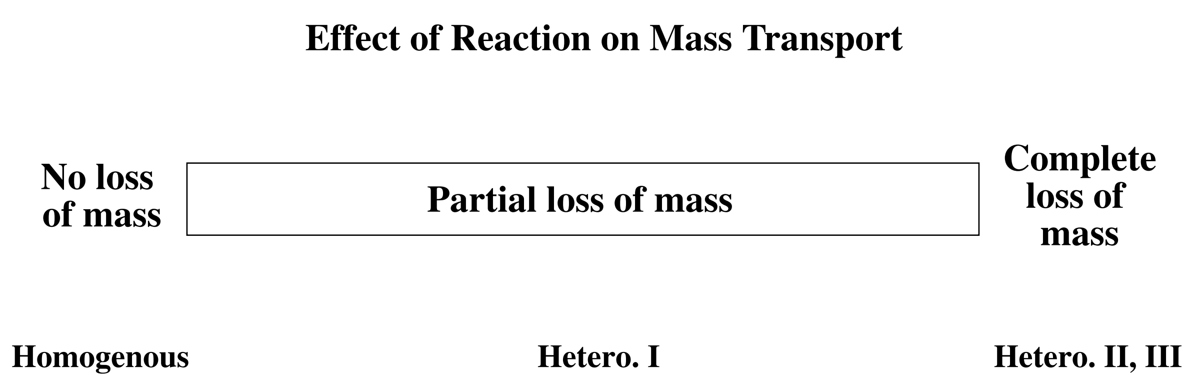


Figure 14: Effect of reaction on mass transport, depicted as a continuum.

The final reaction type, Heterogenous I, falls within the endpoints of the spectrum as it results in a partial loss of mass. For a Heterogenous I reaction, dissolved species interact with solids within the water column and continue to move in the downstream direction. Some of the mass involved in the reaction will be lost, however, as the force of gravity causes the solid to settle to the streambed over time. This loss is dependent on the nature of the solid. The surface area, surface charge and mass of some solids will be such that the losses due to settling are negligible. In this case, the reaction lies to the left end of the spectrum and the net effect is similar to that for a homogeneous reaction. Other solids are such that the rate of settling is significant, resulting in a substantial loss of mass.

The example presented above illustrates the effects of geochemical reactions on transport. As noted in the beginning of this section, this coupling between processes is bidirectional; transport processes also affect the degree to which chemical reactions take place. For example, consider an acidic stream such as the Snake River in which considerable concentrations of dissolved iron are present in the water column. As a parcel of water moves downstream, it may mix with waters of a higher *p*H, as with the case where tributary inflows add nonacidic waters to the stream. As a result of this mixing, the *p*H of the water will increase, and the solubility product for ferrihydrite may be exceeded, resulting in the formation of particulate iron in the water column. Given sufficient time and constant *p*H, these particulates will settle to the streambed and discontinue their downstream movement. Alternatively, the particulates may move farther downstream and encounter additional inflows that are acidic. If mixing results in a decrease in *p*H, the particulates may redissolve rather than settling to the streambed. Transport processes thus result in a dynamic system wherein a parcel of water may be subject to a variety of geochemical regimes over time.

Quantitative analysis of the coupling between physical transport and geochemical reaction may be considered by adding terms to the advection-dispersion equation that represent the effects of chemistry. Numerous formulations of this approach are possible given the different reactions under study and the relative rates of chemical reaction and hydrologic transport. As an example, we consider the sorption of solutes on to the bed of a stream. Two modified formulations of the constant parameter advection-dispersion equation [Equation (11)] are presented. Both formulations assume reversible sorption reactions that are aptly described by the linear form of the Freundlich isotherm [Equation (26)]. First, consider the case where the time scales of reaction are such that sorption may be modeled as an equilibrium process. The corresponding advection-dispersion-reaction equation is given by:

$$\frac{\partial C}{\partial t} = -U\frac{\partial C}{\partial x} + D_L\frac{\partial^2 C}{\partial x^2} - \rho\frac{\partial S}{\partial t} \tag{27}$$

where S is the mass of solute sorbed per mass of sorbent [M/M], ρ is the mass of sorbent per volume of stream water [M/L^3] and,

$$\frac{\partial S}{\partial t} = K_d\frac{\partial C}{\partial t} \tag{28}$$

The effect of sorption on the dissolved solute concentration (C) is embodied in the last term of Equation (27). If sorption is occurring, mass on the streambed will increase ($\partial S/\partial t > 0$) and mass will be lost from the dissolved phase. Conversely, if desorption is occurring, mass on the streambed will decrease ($\partial S/\partial t < 0$) and mass will be added to the dissolved phase. A similar formulation for modeling groundwater systems is presented by *Pickens and Lennox* [1976].

The above equations are applicable when the rate of sorption/desorption is high, relative to the flow velocity of the stream. As such, sorption/desorption is modeled as an instantaneous process. In many situations the assumption of instantaneous equilibrium is not warranted, due high flow velocities and the fact that not all of the solute mass in the water column has access to the sorbent surfaces on the streambed. This case requires a kinetic approach, as given by the following advection-dispersion-reaction equation:

$$\frac{\partial C}{\partial t} = -U\frac{\partial C}{\partial x} + D_L\frac{\partial^2 C}{\partial x^2} - \rho\lambda\,(K_d C - S) \qquad (29)$$

where λ is a first-order rate constant for sorption [/T]. The last term in Equation (29) describes the effect of sorption/desorption as a function of the gradient between the mass sorbed at equilibrium, K_dC, and the mass present on the streambed, S. If the equilibrium amount exceeds the amount present on the bed ($K_dC > S$), sorption takes place and mass is lost from the dissolved phase at a rate that is proportional to λ. Desorption occurs when the amount present on the bed is greater than the amount that would be present at equilibrium ($S > K_dC$). An example of the kinetic approach for sorption/desorption is presented by *Bencala* [1983].

Summary

In this chapter we have discussed many of the processes that effect the fate and transport of solutes in stream ecosystems. We began our discussion with a quantitative look at the physical processes affecting solutes. To broaden our analysis, we also presented several potential geochemical processes that act to transform solute mass and alter species composition. We then described the complex interaction or coupling between the physical processes and the geochemical reactions. In doing so, our purpose was to point out that a variety of processes control solute concentrations, and that emphasis on any one process may result in inaccurate conclusions. Thorough understanding of the system requires an analysis of the coupled processes. Within this chapter, we have presented a primarily qualitative analysis of this coupling. A more rigorous and quantitative analysis requires the use of mathematical models such as those presented by several authors [*Chapman*, 1982; *Bencala*, 1983; *Wood and Baptista*, 1993; *Runkel et al.*, 1994].

Another important consideration is the temporal and spatial variability in the sources of solutes to the stream. This variability contributes to the complexity and dynamics of the system and must be considered within a given solute transport problem. From our study of solute sources, it is evident that the stream is intricately linked with the surrounding watershed. As such, the watershed is a source of both water and solute mass. As pointed out by *Bencala* [1993], the stream is not merely a pipe conveying water downstream, but rather a complex system that interacts closely with the watershed. Consideration of the entire system is thus of paramount importance.

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