Chapter 30

Conservative and Reactive Solute Dynamics

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30.1 INTRODUCTION

Solutes are materials that are chemically dissolved in water. These include cations (positively charged ions) such as calcium, magnesium, sodium, and potassium; anions (negatively charged ions) including chloride, sulfate, silicate, and bicarbonate; and organic molecules. In comparison to these common solutes, which are found in relatively large concentrations in many natural waters, more biologically important solutes such as phosphate and ammonium are normally present at very low concentrations. Solutes enter streams from three natural sources. First, the atmosphere (e.g., rainwater) is often the major source of chloride, sodium, and sulfate. Second, other solutes come from soil and rock weathering, including calcium, phosphate, silica, and magnesium. Third, biological processes may be important. For example, while nitrate may enter from the atmosphere or from weathering, it also may be generated from nitrogen that was biologically fixed by cyanobacteria. In addition, inorganic carbon (i.e., carbon dioxide, bicarbonate, or carbonate) comes from the atmosphere and weathering, but it also comes from respiration by soil and stream organisms. Point sources (such as pipes) and nonpoint sources (e.g., agricultural runoff) are often major inputs of solutes to streams.

Solutes in water can be classified according to their biological and chemical reactivity. *Conservative* solutes are those that do not react chemically or biologically, and thus their concentration is not changed by in-stream processes other than dilution from groundwater or tributaries. As such, conservative solutes mimic downstream transport of water. Examples of conservative solutes include lithium and bromide (e.g., Bencala et al., 1991). On the other hand, solutes whose concentration is changed by chemical and/or biological transformations are referred to as nonconservative or *reactive* solutes. Nutrients such as nitrate and phosphate are examples of reactive solutes. Some reactive solutes may be so abundant that biological and chemical transformations do not measurably influence stream concentration and may in fact be treated as conservative solutes. Chloride is an example of such a solute that, although is essential to organisms, exists in most streams in concentrations that far exceed biological needs. As such, chloride is often used as a conservative solute in stream studies (e.g., Triska et al., 1989).

Solute dynamics describe the coupled physical, chemical, and biological processes that govern transformations of materials dissolved in water. As such, the term describes the spatial and temporal patterns of solute transport and transformation (Stream Solute Workshop, 1990). Solute dynamics are tightly coupled to the physical movement of water in all ecosystems, but in streams this coupling between transport and transformation is particularly important. Material cycling in a conventional, ecological, sense describes the continued recycling of solutes between inorganic and organic (living or dead) forms (Fig. 30.1). When considering a single point in space and time, the unidirectional flow of stream water prohibits material cycling in this conventional view (Webster and Patten, 1979). At the reach scale, however, cycling becomes apparent as inorganic materials are mineralized and transported downstream before being reacted upon biologically or chemically. Stream ecologists term this combination of cycling and longitudinal transport a *spiral* (Fig. 30.1; Webster, 1975). The balance between how much and for how long solutes are retained versus being transported longitudinally is central to understanding stream ecosystem functioning.

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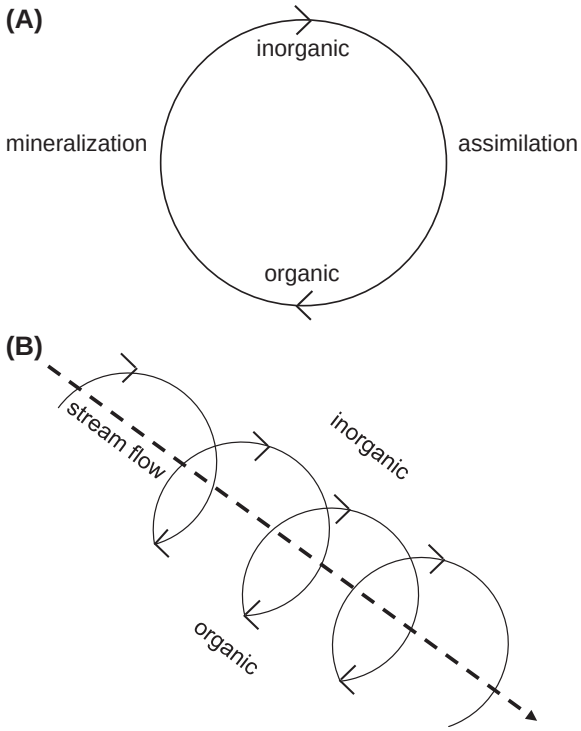

FIGURE 30.1 (A) Simple nutrient cycle and (B) nutrient spiral depicting longitudinal transport as well as cycling between inorganic and inorganic forms. *After Newbold (1992).*

While the dynamics of many solutes are determined primarily by biogeochemical and hydrologic interactions occurring in the whole watershed (Webb and Walling, 1992), important in-stream dynamics also occur (e.g., Peterson et al., 2001; Bernhardt et al., 2003). Studies of solute dynamics in streams provide two types of information. First, dynamics of conservative solutes can be used to quantify various hydrodynamic properties of a stream reach or segment. Second, comparing conservative and reactive solute dynamics can provide information on rates of transport and transformation of the solutes themselves, which is important to the understanding of their availability and importance. In this chapter, we describe investigations of solute dynamics from both perspectives.

30.1.1 Conservative Solute Dynamics

The dynamics of conservative solutes in streams are driven largely by two processes—advection and dispersion. *Advection* is downstream transport of the solute with the water itself, occurring at average water velocity. *Dispersion* is the spreading of the solute in the medium and can occur by molecular diffusion, but in streams diffusion is primarily caused by turbulence. Dispersion allows some solute molecules to move more rapidly or more slowly than the bulk transport of materials due to advection. Mathematical models derived from the advection−dispersion equation are used to quantify solute dynamics in streams (Bencala and Walters, 1983; Stream Solute Workshop, 1990). These models can take on varying degrees of complexity depending on what aspects of solute dynamics are being considered. The following description was adapted from the more complete derivations presented in the Stream Solute Workshop (1990).

For a uniform channel with constant discharge, advection and dispersion can be expressed in the partial differential equation

$$\frac{\partial C}{\partial t} = -u\frac{\partial C}{\partial x} + D\frac{\partial^2 C}{\partial x^2} \tag{30.1}$$

where C = solute concentration; t is time; x = distance in the downstream direction; u = water velocity; and D = dispersion coefficient. This equation means that the rate of change in concentration with time is a function of advection plus dispersion in the downstream (x) direction. Other terms can be added to this equation to include variable stream morphology, groundwater inputs, and transient storage. *Transient storage* refers to the temporary storage of water that is traveling much more

slowly than the main body of water (Bencala and Walters, 1983), such as water in hyporheic flow paths, surface pools or backwaters, and macrophyte beds (e.g., Bencala et al., 1984; Harvey et al., 1996; Ward, 2015). Adding these factors, the mathematical model becomes a pair of equations:

$$\frac{\partial C}{\partial t} = -\frac{Q}{A}\frac{\partial C}{\partial x} + \frac{1}{A}\frac{\partial}{\partial x}\left[AD\frac{\partial C}{\partial x}\right] + \frac{Q_L}{A}(C_L - C) + \alpha(C_S - C)$$

and (30.2)

$$\frac{\partial C_S}{\partial t} = -\alpha\frac{A}{A_S}(C_S - C)$$

where Q = discharge; A = stream cross-sectional area; Q_L = lateral inflow from groundwater; C_L = solute concentration of the lateral inflow; α = exchange coefficient between the main channel and transient storage zones; A_S = size (cross-sectional area) of the transient storage zone; and C_S = solute concentration in the transient storage zone. The first equation is the advection–dispersion equation (as in Eq. (30.1), but allowing for changes in stream discharge and cross-sectional area) with lateral inflow and transient storage, while the second equation describes the rate of concentration change in the transient storage zone as a function of exchange rate and the size of the storage zone relative to the main channel (both as cross-sectional area). Metrics to compare transient storage among streams can be derived from these parameters and include A_S/A (from Eq. 30.2) and F_{med} (the fraction of median transport time in transient storage) along with others (e.g., Harvey and Wagner, 2000; Runkel, 2002).

30.1.2 Reactive Solute Dynamics

Dynamics of reactive solutes are more complicated because of the production and consumption of these solutes by in-stream processes. In streams, the majority of these processes occur on the stream bottom, although processes in the water column also can play a role (Reisinger et al., 2015). Such processes may be abiotic, such as adsorption, desorption, precipitation, and dissolution. Many biotic processes, such as assimilation by microbes and plants, as well as mineralization, are important to the dynamics of reactive solutes in streams. Generally, abiotic and biotic processes that remove solutes from the water column are termed *immobilization*. In streams the most important immobilization processes for nutrients are adsorption (especially for phosphate) and microbial uptake (by heterotrophs and algae). Revising the advection–dispersion equation for uniform channel and discharge to account for immobilization, the expression becomes:

$$\frac{\partial C}{\partial t} = -u\frac{\partial C}{\partial x} + D\frac{\partial^2 C}{\partial x^2} - \lambda_C C \tag{30.3}$$

where C = reactive solute concentration, λ_C = dynamic uptake rate (units of time^{-1}), and the other terms are as described for Eq. (30.1). Nutrients that are immobilized will eventually be mineralized and returned to the water column. This can be most simply expressed by adding another term to Eq. (30.3) and adding another equation for the immobilized nutrient:

$$\frac{\partial C}{\partial t} = -u\frac{\partial C}{\partial x} + D\frac{\partial^2 C}{\partial x^2} - \lambda_C C + \frac{1}{z}\lambda_B C_B$$

and (30.4)

$$\frac{\partial C_B}{\partial t} = z\lambda_C C - \lambda_B C_B$$

where C_B = immobilized nutrient standing crop (usually considered to be benthic, as mass per unit area), z = stream depth, and λ_B = rate of mineralization.

As a nutrient atom cycles between inorganic and organic forms (Fig. 30.1), the spiraling length (S) is the distance it travels while completing this cycle (Newbold et al., 1981; Elwood et al., 1983). Over the length of a spiral, the nutrient changes from abiotic to biotic and back to abiotic form. Thus, the spiraling length has two components: (1) the *uptake length* (S_W) is the distance traveled in dissolved inorganic form before the nutrient is removed from solution, and (2) the *turnover length* (S_B) is the distance traveled before being mineralized and returned to the water column:

$$S = S_W + S_B \tag{30.5}$$

Because much of the organic material in streams resides in the benthic sediments (e.g., Fisher and Likens, 1973) and movement of these particles is far slower than movement of dissolved constituents (Newbold et al., 1983; Minshall et al., 2000), the uptake length dominates total spiraling length (Newbold et al., 1983; Mulholland et al., 1985). Accordingly, we focus on dynamics of dissolved inorganic nutrients as addressed by S_W and related measures.

Uptake length can be mathematically related to Eqs. (30.3) and (30.4) as the inverse of the longitudinal uptake rate:

$$S_W = \frac{1}{k_W} \tag{30.6}$$

where the longitudinal uptake rate (k_W) is the dynamic uptake rate (λ_C) divided by water velocity:

$$k_W = \frac{\lambda_C}{u} \tag{30.7}$$

Because S_W is a displacement distance, it is strongly influenced by stream discharge and velocity. To correct for this influence of stream size, S_W is often standardized to allow comparison of solute dynamics across systems (Davis and Minshall, 1999). This standardization converts S_W to a mass transfer coefficient, which describes a theoretical velocity at which a nutrient moves toward the location of immobilization (Stream Solute Workshop, 1990). This mass transfer coefficient is referred to in the literature as the uptake velocity (v_f, Davis and Minshall, 1999). Uptake velocity is related to the uptake rate coefficient (k_C) through stream depth (z) as $v_f = zk_C$. As such, v_f is related to S_W and can be calculated as:

$$v_f = \frac{uz}{S_W} \tag{30.8}$$

In some instances, it is useful to describe nutrient uptake per unit area of stream bottom (mass area^{-2} time^{-1}), as is done in other ecosystems. Areal uptake (U) is calculated as:

$$U = v_f C \tag{30.9}$$

where C = ambient nutrient concentration. *Areal uptake* refers to the mass of solute immobilized by an area of streambed per unit time and reflects the magnitude of the flux of inorganic solute from the water column to the biota. In the literature, U is sometimes referred to as "uptake rate"; however, this is inaccurate—the units of U represent a transport flux—in this case the mass of solute flow across a unit area. Stream ecologists use the term "uptake" synonymously with immobilization. Certain uptake processes may be assimilatory while others may be dissimilatory (e.g., denitrification) or abiotic (e.g., adsorption). It is important to note that U represents gross uptake and not net retention, as mineralization releases some portion of nutrients back to the water column (Stream Solute Workshop, 1990).

Together, these measures (S_W, v_f, and U) provide insight into the dynamics of nutrients in streams, and these metrics are mathematically related (Fig. 30.2; Webster and Valett, 2007). Uptake length is a reach- or segment-scale estimate of retention efficiency and gives explicit information (as distance) about the spatial extent over which nutrient uptake occurs. Areal uptake conveys important information on biological assimilation or other immobilization processes and is useful for comparison with other ecosystems but does not provide this spatial context. Uptake velocity standardizes uptake length for discharge (depth and velocity). Uptake velocity is also a measure of nutrient demand (areal uptake) relative to nutrient availability (Davis and Minshall, 1999), as seen by rewriting Eq. (30.9) as:

$$v_f = \frac{U}{C} \tag{30.10}$$

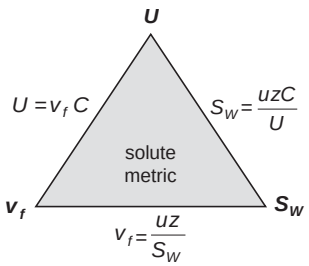

FIGURE 30.2 Metric triad for determining nutrient dynamics in stream ecosystems. Symbols are defined in the text. *After Webster and Valett (2007).*

Conceptually, S_W is useful as an overall index of nutrient retention by streams because it accounts for physical transport processes leading to export and biogeochemical processes that retain nutrients in the stream for some time. S_W increases with stream discharge (Peterson et al., 2001; Tank et al., 2008; Hall et al., 2013) and decreases with autotrophic processes (e.g., Hall and Tank, 2003) and heterotrophic processes (Mulholland et al., 1985) as microbes that mediate both types of processes require nutrients for their activities. Stream substrates with greater surface area and/or higher biofilm biomass may also decrease S_W (Davis and Minshall, 1999; Arp and Baker, 2007). Shorter uptake lengths are expected for nutrients that limit biological processes (Newbold et al., 1983; King et al., 2014).

Because of the influence of stream discharge on S_W, v_f and U are better metrics for assessing the influence of nutrient concentrations and biomass on nutrient uptake (Stream Solute Workshop, 1990; Davis and Minshall, 1999; Dodds et al., 2002). Three models describing the relationship between uptake and concentration have been proposed. The first is a linear relationship between nutrient concentration and U (Dodds et al., 2002; O'Brien et al., 2007). Under this scenario, U increases linearly with concentration, and mass transfer across a stream-averaged boundary layer limits uptake according to the equation:

$$U = kC \tag{30.11}$$

where k = constant and C = ambient concentration (Dodds et al., 2002).

At the other extreme, the relationship between uptake and concentration may be controlled by reaction kinetics and follow a Michaelis–Menten type model (Stream Solute Workshop, 1990; Bernot and Dodds, 2005). In this case, the relationship between U and concentration is hyperbolic and reaches a saturation point above which U no longer increases with concentration. Mathematically this model is of the form:

$$U = \frac{C_b U_{max}}{K_m + C_b} \tag{30.12}$$

where U = areal uptake, C_b = background concentration, U_{max} = maximum uptake rate, and K_m = Michaelis, or half-saturation, constant. By substitution, the Michaelis–Menten model predicts a positive linear relationship between S_W and concentration and a negative nonlinear relationship between v_f and concentration (Earl et al., 2006, 2007).

A third model, termed the Efficiency Loss model, is similar to the Michaelis–Menten model in that the relationship between uptake and concentration is nonlinear. It suggests that as concentrations increase, the efficiency of uptake decreases such that the relationship between U and concentration is a power law with exponent (b) less than one:

$$U = kC^b \tag{30.13}$$

In this scenario, S_W increases nonlinearly with concentration while v_f decreases nonlinearly with concentration (O'Brien et al., 2007).

These models have been tested at the reach scale with regard to *P* uptake and *N* uptake (as ammonium and nitrate; Dodds et al., 2002; Bernot et al., 2006; Earl et al., 2006; Newbold et al., 2006; O'Brien et al., 2007). For nitrate, uptake appears to follow Michaelis–Menten kinetics for many streams, but the Efficiency Loss model better explains data across Kansas streams that vary widely in *N* loads (O'Brien et al., 2007). In contrast, nitrate uptake attributable to denitrification has a first-order (linear) relationship with concentration, suggesting that if substrate is available, denitrification is limited by mass transfer (O'Brien et al., 2007; Mulholland et al., 2008). For oligotrophic streams, the Michaelis–Menten model tends to best fit observed data for ammonium or phosphate uptake (e.g., Payn et al., 2005; Bernot et al., 2006; Newbold et al., 2006).

The experiments described in this chapter allow exploration of dynamics of both conservative and reactive (nutrient) solutes in flowing waters. Because of differences in equipment that might be available and the highly variable nature of stream chemistry, we have provided a number of procedural options. At a minimum, you should be able to measure discharge, velocity, the importance of transient storage, and estimate nutrient uptake. The procedure for estimating nutrient uptake described here requires elevating nutrient concentration. Because uptake rate (k_C) is proportional to concentration, experiments that increase concentrations above ambient conditions tend to overestimate S_W (Mulholland et al., 2002; Dodds et al., 2002). Isotopic tracers such as ^{15}N and ^{32}P do not elevate nutrient concentrations and therefore provide the most accurate estimates of nutrient update. The stable isotope ^{15}N has been widely used to study *N* cycling in streams (e.g., Peterson et al., 2001; Mulholland et al., 2008)—its major limitation being economic. The radioisotope ^{32}P was used as a tracer in the pioneering work of Elwood et al. (1981), but this tracer is not feasible for use in most environments because of its radioactivity. See Chapters 31 and 32 for procedures involving isotopes.

Alternatives to nutrient enrichment procedures include sequential addition of nutrients at increasingly higher concentrations (Payn et al., 2005; Earl et al., 2007; Demars, 2008) and back-calculating nutrient uptake metrics at ambient

concentration. While more effort is needed, this approach not overestimate S_W. A more recent alternative is the Tracer Additions for Spiraling Curve Characterization (TASCC) approach (Covino et al., 2010), which involves using an instantaneous pulse of concentrated solutes to take advantage of the dynamic concentration range observed at a single location as the solutes move through a stream reach. Each data point along the breakthrough curve (BTC) is used to estimate S_W and net areal uptake at each concentration of nutrient compared to a conservative solute. These data then can be used to estimate functional relationships across a range of concentrations in a manner similar to that initially proposed by Payn et al. (2005) for plateau tracer tests. It is beyond the scope of this chapter to describe and compare multiple methods for measuring nutrient uptake metrics in the field (but see Alvarez et al., 2010; Trentman et al., 2015 for a comparison of approaches) and for discussion of the various reactive transport models (e.g., Runkel, 2007; Payn et al., 2008; Claessens and Tague, 2009) that can be used to solve for nutrient uptake metrics. Several studies have also used nutrient declines downstream of point sources such as wastewater treatment plants or springs to estimate nutrient removal (e.g., Gibson and Meyer, 2007; Hensley et al., 2014). However, this technique measures net nutrient removal and the difference between gross uptake and mineralization and provides less insight into nutrient dynamics occurring in the stream. These measurements of net nutrient removal can be useful in determining the capacity of a stream to remove dissolved nutrients from downstream transport by processes such as denitrification, but net nutrient removal cannot be directly compared with measurements of uptake described in this chapter.

Here, we provide a general field-based approach to study conservative and reactive solute dynamics using pulse and steady-state (plateau) approaches. The general approaches described here could subsequently be used for more advanced analyses such as sequential nutrient or stable isotope releases, TASSC analysis, and/or solute transport modeling.

30.2 GENERAL DESIGN

The general design of these experiments involves releasing a known concentration of solute either as a pulse (instantaneous release) or at a constant rate (plateau release) and making measurements at a downstream location. Care should be taken in site selection, choice of solute(s), method of release, and data analysis as described below.

30.2.1 Site Selection

Nearly 1000 solute releases have been performed in first- to fourth-order streams that range in discharge from <1 to 2000 L/s (Tank et al., 2008; Hall et al., 2013). Streams of this size allow wadeable access for physical measurements and sampling, and most of these studies have used constant-rate releases. At larger stream flows, the pulse release method and sampling design are preferred for logistical reasons (e.g., Dodds et al., 2008; Tank et al., 2008).

Choice of a stream or section of stream will depend on the question posed (e.g., single reach or comparison of multiple reaches). Ideally, a stream or set of streams should be selected that provide a range of physical and biological conditions. A comparison of hydraulic properties between two reaches might include one simple reach (e.g., straight channel, homogenous substrate, low amount of wood) and one more complex reach (e.g., sinuous channel, heterogeneous substrate, high amount of wood). Avoid reaches with tributary inputs or water diversions. Experimental reach length will vary with flow (higher flows require longer reaches), but reach length must be long enough for complete mixing of the released solute(s). Complete mixing can be evaluated using a preliminary dye release (e.g., Rhodamine WT or fluorescein) and visual observation. Typical reach lengths range from 50 m for small headwater streams to several hundreds of meters for mid-order streams, or to several kilometers for rivers.

30.2.2 Tracer Selection

Selection of a conservative solute is a function of local geology, ambient solute concentration, research budget, and analytical capacity. It is essential to raise stream concentration of the solute sufficiently above ambient concentration to be analytically detectable, while avoiding potential harm to biota (e.g., Flury and Papritz, 1993; Stewart and Kzsos, 1996). A number of hydrological studies have used the dye, Rhodamine WT, as a conservative tracer, but recent research (Runkel, 2015) shows that Rhodamine WT can sorb to hyporheic sediments and thus exhibits nonconservative behavior and should not be used to characterize transient storage processes. Typical conservative solutes used are salts of chloride, sodium, lithium, potassium, and bromide. Of these, chloride is the most common. Chloride can easily be obtained as NaCl at a grocery store or feed store, but choose a noniodized form. Most commercial NaCl contains a small amount of cornstarch or other anticaking agent, which will cause a slightly cloudy solution but should not be a problem. Chloride measurements in the field can be made conveniently with a conductivity meter, and conductivity itself can be used as a conservative measure (e.g., Mulholland et al., 1994).

Conductivity is very sensitive to temperature, but most handheld meters and data sondes can be set to measure specific conductance, which corrects for temperature. Portable ion-specific electrodes also are available for

chloride, bromide, sodium, and other ions. Bromide has the advantage of very low ambient concentrations in most waters (e.g., Flury and Papritz, 1993) and may be preferred in streams where ambient chloride concentrations are high. A disadvantage to using sodium as a conservative tracer is that it loses 5−10% by mass through sorption to stream bottom materials compared to almost no loss of chloride (Bencala, 1985). A disadvantage to using ion-specific electrodes is that they are sensitive to matrix effects; bromide electrodes are influenced by variations in ambient chloride, for example. Both conductivity sensors and ion-specific electrodes can be calibrated using solutions prepared with water from the study stream for better performance. If portable instruments are not available, samples can be collected and filtered in the field and then analyzed by ion chromatography or other means in the laboratory.

One or more reactive solutes (e.g., nutrients) can be added along with a conservative solute to estimate uptake metrics. Choice of a nonconservative solute for study will depend on your specific research objectives and knowledge of the streams of interest. If choosing a nutrient, phosphate and inorganic forms of nitrogen (nitrate or ammonium) are obvious candidates. Your choice may depend on the availability of analytical instrumentation for measuring concentrations of these nutrients. Be sure not to choose a nutrient that will interact with the conservative solute. For example, calcium and phosphate cannot be used together because they form a highly insoluble salt. Also take care to choose nonconservative solutes that do not interfere with analysis and interpretation of data. For example, nitrate and ammonium should not be used together if nitrification is an important process because nitrate uptake could be masked to an extent by nitrate produced by nitrification.

30.2.3 Release Techniques

In this chapter, we describe techniques for two types of solute releases. The first is the slug release, also termed a gulp or pulse release. In this method, a preweighed mass of salt is dissolved in stream water, and the entire volume is dumped nearly instantaneously at an upstream location. Concentration of solute at a site downstream is measured as a function of time until the concentration recedes to ambient levels (Fig. 30.3). This method can be used to estimate discharge (dilution gauging; see Chapter 3) or used for analyses of solute dynamics.

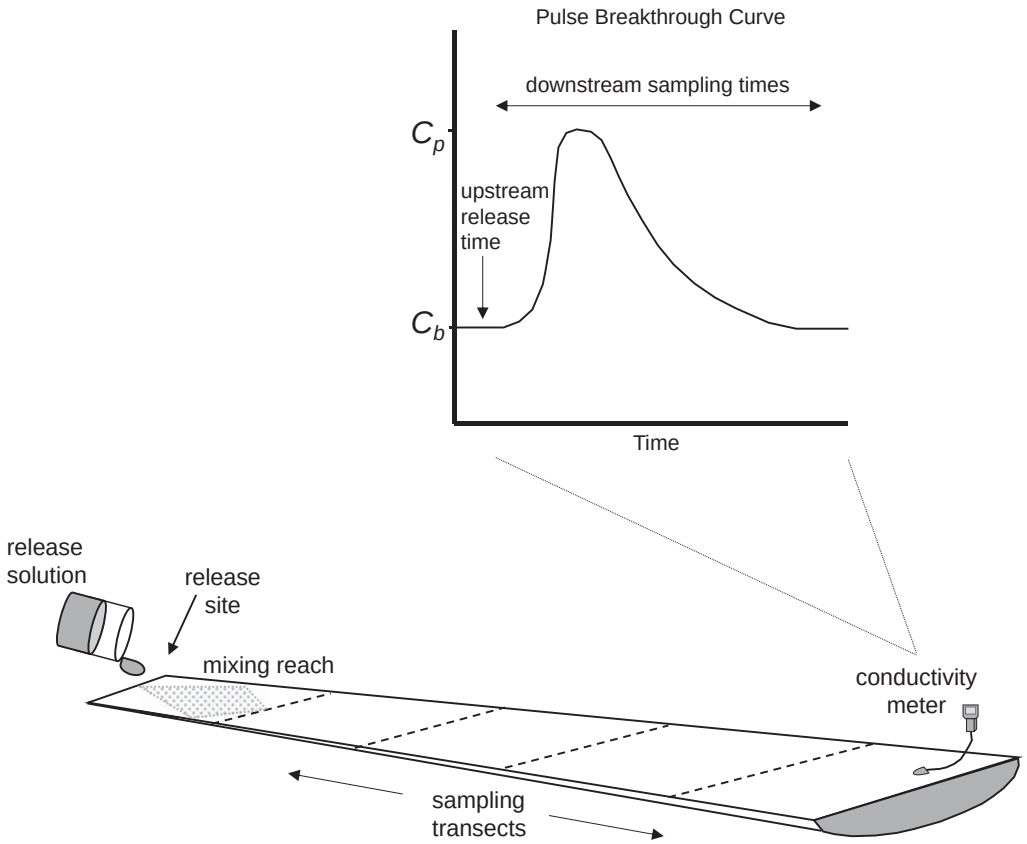

FIGURE 30.3 Diagram of setup for a pulse release and an idealized breakthrough curve for a pulse release of conservative solute. C_b = background concentration, C_p = peak concentration. See also Online Worksheet 30.1.

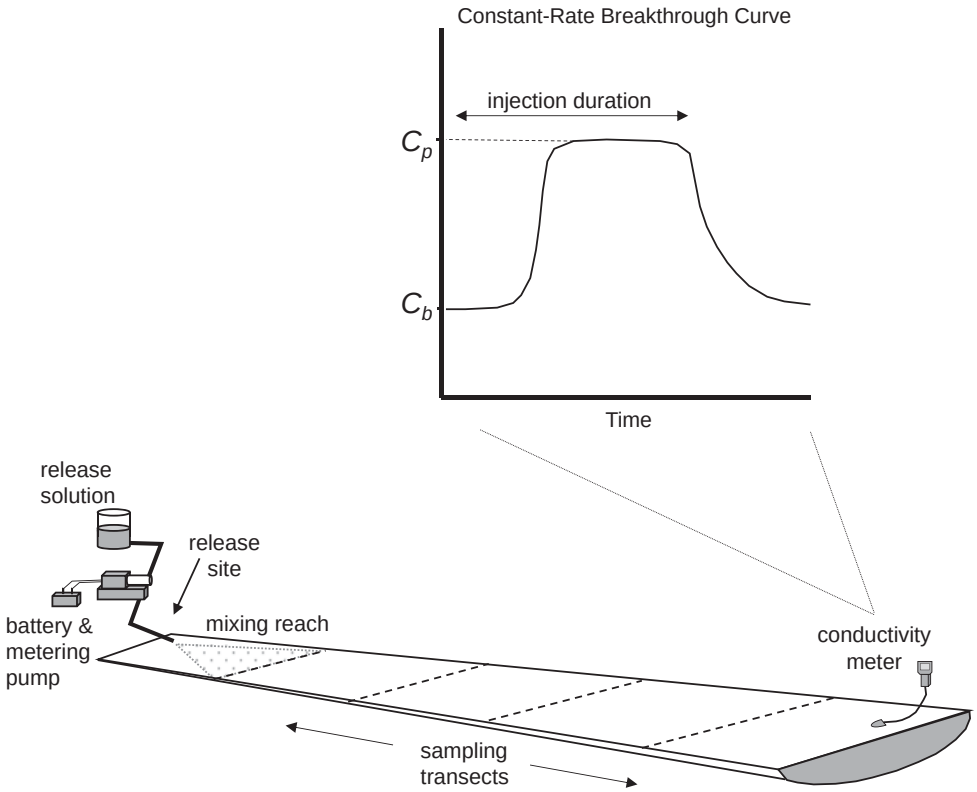

FIGURE 30.4 Diagram of setup for a constant-rate release and an idealized breakthrough curve for a constant release of conservative solute. C_b = background concentration, C_p = plateau (peak) concentration. See also Online Worksheet 30.1.

Constant-rate releases are useful for measuring solute dynamics in small streams and are advantageous over pulse releases in which fewer samples are required for laboratory analysis. In this technique, solutes are dissolved in stream water and then added at a constant rate to the stream for some time period until the added solute concentration reaches a plateau above ambient concentration at a downstream site (Fig. 30.4). A simple, inexpensive, and nonelectrical release apparatus is the Mariotte bottle (Webster and Ehrman, 1996); however, battery-powered metering pumps (e.g., Fluid Metering, Inc., Syosset, NY, USA) are generally more reliable, and pump rates can be easily adjusted to field conditions. At discharge above 2000 L/s it is challenging to pump sufficient solute(s) to the stream using this technique, and the pulse method would be preferred.

30.2.4 Data Analyses

The most important data to be collected and analyzed during a solute tracer test is a concentration-time profile at one or more downstream locations from the point of release. This profile is called a *breakthrough curve*. Beyond the single reach release, solute dynamics can be compared spatially among the reaches of one to several streams, before and after manipulation, and over time at different flows. Reactive solute (nutrient) releases can be performed simultaneously with conservative tracer, and the BTCs for both solutes simulated and compared.

Essential physical measurements to be made in studies of solute dynamics include ambient water chemistry (especially for the solutes that are to be used as tracers), water temperature, stream discharge, average water depth, and average wetted-channel width for the stream reach over which the release is being conducted (see Chapters 2–5). These data should be included in any publication so that the published data set is useful for future syntheses and metaanalyses. A number of other potentially interesting and important measurements that can be made to aid in interpretation are described elsewhere in Volumes 1 and 2 of this book, including, for example, thalweg velocity (Chapter 4), gradient (Chapter 2), sediment size distribution (Chapter 5), coarse wood volume or area (Chapter 29), benthic biomass (Chapter 12), and metabolism (Chapter 34).

One can calculate hydraulic characteristics such as discharge and velocity by graphical analysis of the BTC resulting from the experiment; however, it is necessary to have a reasonable estimate of discharge prior to the experiment to calculate expected solute release concentrations. If one has a measurement of discharge independent of the BTC data, tracer recovery can be calculated, which can give insight into losses of water from the main channel to the subsurface (e.g., Payn et al., 2009). Uptake length and rate can be calculated from nutrient data fit to a negative exponential model. For each solute release, a computer model can be used to simulate the observed BTC and calculate hydraulic parameters such as dispersion and transient storage size and exchange rate. These techniques are described later in this chapter.

30.3 SPECIFIC METHODS

30.3.1 Basic Method: Dynamics of Conservative Solutes

In this exercise, we use chloride as the conservative solute and derive concentration from data obtained with a temperature-correcting specific conductance meter. For brevity we call this conductivity. We describe laboratory and field preparations to be done prior to conducting conservative solute tracer tests in the field as well as two field techniques—a slug (pulse) release and a constant rate (plateau) release.

30.3.1.1 Laboratory Preparation

1. Prepare a stock solution of sodium chloride in deionized or distilled water. A stock solution of 238 g NaCl/L (144 g Cl/L) is two-thirds the saturation of NaCl in cold water and is fairly easily dissolved. The mixture can be heated in a water bath to aid dissolution. Mix vigorously and repeatedly to be certain that the salt is completely dissolved.
2. Make serial dilutions from the stock solution to prepare a series of chloride standards across the range of expected chloride concentrations (e.g., 0.25−20 mg/L). The standards can be made by diluting the stock solution in deionized water, but could also be made by diluting the stock solution in stream water. The latter is generally more accurate especially if there are matrix effects or if ionselective probes are used to collect data.
3. Large volumes of stock solution could be prepared to use in the field for releases. Alternatively, the salt can be preweighed in 500-g increments into labeled zipper top plastic bags and used to prepare tracer solutions stream side.

30.3.1.2 Field Preparation—Prerelease

1. In the field, walk the intended study reach, and identify the location of the release site above a good mixing reach. A good mixing reach is one that is not wide and slow-moving, rather above a small riffle or swift moving water would help mix the tracer laterally and vertically. Identify the location of the end of the study reach where the conductivity meter will be deployed.
2. Place the chloride standards in the stream to equilibrate with ambient stream temperature. Calibrate the conductivity meter with the standards per the manufacturer's instructions.
3. Use a tape measure to delimit the extent of the study reach between the release point and end of study reach. Mark every 5 m (for a 100-m reach) with labeled flagging tape. At each 5-m transect, measure wetted-channel width, depth (c.10 measurements at each cross section), and thalweg velocity (optional). Often, "effective depth" calculated from discharge, velocity, and width will be more useful than measured depth (see Chapter 34). Additional data such as benthic biomass, substrate size distribution, and gradient could also be collected at these locations.
4. Measure stream flow at the top and bottom of the stream reach using the velocity−area method or other means as described in Chapter 3.
5. For constant-rate releases, working in a downstream−upstream direction, measure stream temperature and ambient chemistry (either with the conductivity meter or by collecting a grab sample from the thalweg) every 10 m.
6. For both release types, place the conductivity meter in a well-mixed area at the downstream site, and assign a person to record conductivity during the release. Synchronize stopwatches among all team members (and the conductivity meter if it automatically records data). For pulse releases, collect several measurements of temperature and ambient chemistry (conductivity) before the release.

30.3.1.3 Field Procedure—Pulse Release

1. For a pulse release, prepare the tracer solution in a 5-gallon (~20-L) bucket at the top of the reach. Either use a preprepared solution or dissolve a known mass of salt using 2.5 gallons (~10 L) of stream water. For conductivity, it may be sufficient to increase stream concentration by 10 µS/cm if the conductivity meter reads to 0.1 µS. We have found that a mass of 500 g NaCl can increase the peak conductivity by about 50 µS/cm in a stream flowing at 100 L/s, but this depends on transport characteristics and dilution along the reach. Make sure to record the mass of salt and volume of water added to the bucket. A small (1 mL or less) aliquot of tracer solution should be collected to measure concentration of the tracer at a later time.
2. Add the dissolved tracer by quickly pouring the bucket's contents across the width of the stream, and quickly rinse the bucket and mixing stick in the stream. This will ensure that all the tracer mass enters the stream. Be sure to record the time of tracer addition.
3. At the downstream location, record conductivity every minute or two until the tracer pulse begins to arrive, and then increase recordings every 15 s as the conductivity increases rapidly. If using a data sonde or recording meter, set the instrument to record conductivity every 2 s. Collect data in this manner until the tracer completely passes the downstream location and conductivity returns to ambient conditions.

30.3.1.4 Field Procedure—Constant-Rate Release

1. Calculate the release (pumping) rate and solute concentration necessary to raise stream concentration measurably above background for a given flow rate. A target plateau increase of 10 µS/cm may be sufficient as stated above. Use the measured discharge to calculate the release rate (Q_R) as

$$Q_R = \frac{Q \times C_S}{C_I} \tag{30.14}$$

   where Q = stream discharge, C_S = target stream concentration of added solute, and C_I = concentration of the solute in the release solution.
2. At the top of the reach, prepare the release solution at C_I by dissolving the preweighed salt in the appropriate volume of stream water, or use a preprepared solution. Use a sufficiently large volume so that the solution does not run out before plateau is reached at the downstream location. Release duration can be anywhere from 30 min to several hours depending on stream flow and reach length. Make sure to record mass of salt and volume of water used. Reserve a small aliquot (1 mL or less) of tracer solution to verify C_I at a later time.
3. Set up the pump as described by the manufacturer. Set the pump rate to Q_R as calculated above using a graduated cylinder and stopwatch. Make sure to keep a bucket under the release hose to avoid premature tracer addition to the stream. During the release, periodically check and record the release rate as the pump rate can drift over time, and empty the collected solute into the stream.
4. Begin the release by turning on the pump and recording the start time. The person at the downstream site should begin recording conductivity every 1−5 min until the tracer arrives and then every 15 s as conductivity increases rapidly.
5. At plateau, that is, when the conductivity is no longer changing, work in a downstream to upstream direction, and measure conductivity (or collect grab samples) in the stream at 10-m intervals. If you only have one conductivity meter, the break in the data at the downstream site won't be a problem. After taking the upstream measurements, return the meter to the downstream site. Then shut off the release. Record the total time of release (i.e., the duration of the solute addition).
6. Continue recording conductivity at the downstream site until conditions approach background or ambient levels. We have frequently found that conductivity readings never return to background levels, either because of real change in background concentration or because of instrument drift. To correct for either of these problems, it is useful to measure conductivity above the release site several times during the experiment.

30.3.1.5 After the Release

1. Summarize the physical parameters measured in the field [mean width, and depth at each cross section over the whole reach, mean velocity (optional), gradient (optional)].
2. Make a 1:10,000 dilution of the release solution, and measure the conductivity (or chloride concentration). Convert the measured conductivity values to chloride concentration using the known concentrations from the chloride standards.

3. Graph the conservative solute concentration versus time since tracer addition start at the downstream end of the reach—this plot is called a breakthrough curve.

30.3.1.6 Estimating Discharge

1. For a slug release, discharge at the downstream location can be estimated as (see Chapter 3):

$$Q = \frac{M}{\int_0^t C(t)} \tag{30.15}$$

where M = mass of tracer added, C = concentration, and t = time. This equation makes two important assumptions: first, we assume that all of the added tracer was recovered at the downstream sampling location; second, we assume that the added solute was completely mixed across the stream channel where it passed the downstream sampling location.

2. For a constant-rate release, discharge can be calculated as:

$$Q = \frac{(C_R - C_b) \times Q_R}{C_p - C_b} \tag{30.16}$$

where Q_R = release rate; C_R = chloride (or conductivity) concentration of the release solution, C_P = plateau chloride (or conductivity) concentration, and C_b = background (i.e., ambient) chloride (or conductivity) concentration. As for Eq. (30.15) (above), this equation assumes perfect mixing and 100% tracer recovery. Use this equation to calculate discharge at each of the transects where plateau measurements were made. Make a graph of discharge versus distance to see if there is evidence of groundwater input. If there is evidence of a flow increase at a specific point, go back to the stream and see if you can identify landscape features associated with this subsurface input.

3. Compare your estimate of discharge with the direct measurements you made in the field.

30.3.1.7 Estimating Other Hydraulic Parameters

4. Nominal travel time (NTT) for a pulse release is the time required for tracer to reach peak concentration and is the time required for the tracer concentration to reach half of the plateau concentration in the case of constant-rate releases. Using your BTC, estimate NTT.

5. The median travel time (MTT) is another measure of hydraulic retention, defined as the time required for half of the tracer mass to pass out of the stream reach (Runkel, 2002). Tracer mass can be estimated by integration of the BTC:

$$M_{REC} = Q_D \int_0^t C_D(t) \tag{30.17}$$

where M_{REC} = tracer mass recovered at the downstream site, Q_D = measured discharge (this must be an independent measure and not estimated from the tracer test), C_D = concentration at the downstream location, and t = time. Such integration can be done with many graphics or spreadsheet programs, and MTT is the time for 50% of the mass to pass the downstream station.

6. Average solute velocity can be calculated by dividing the length of the reach by MTT. Compare this calculated value with the direct measurements of thalweg velocity made in the field.

7. Once tracer mass recovery has been estimated using Eq. (30.17) (above), it is useful to compare this mass to the mass that was added during the tracer test. Calculate percent recovery as:

$$\%\text{rec} = \frac{M_{REC}}{M} 100 \tag{30.18}$$

where M_{REC} = mass recovered at the downstream sampling station and M = mass added during the tracer test. Compare your recovered mass with the mass you added in this way. If less tracer is recovered than was added, this could represent tracer that entered a flow path that left the main channel and did not return—in other words, a loss of water. This sort of analysis can allow for estimation of water gains and losses along the study reach (Payn et al., 2009).

30.3.1.8 Transient Storage

A number of solute transport models can be used to simulate the BTC, which allow estimation of transient storage parameters (Eq. 30.2). One such model is a program called OTIS (One-dimensional Transport with Inflow and

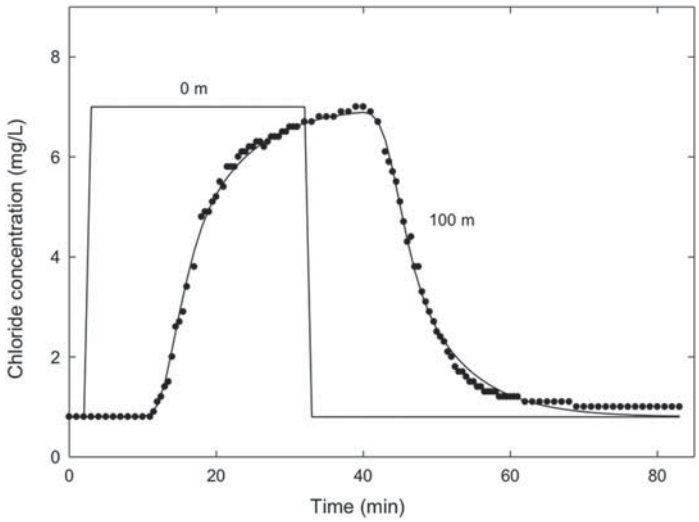

FIGURE 30.5 Breakthrough curve for chloride in a stream with considerable transient storage and no increase in flow over the reach. Square wave at 0 m shows tracer input. At 100 m, the dots are actual data and the solid line is a computer simulation of these data using a transient storage model.

Storage; Runkel, 1998) produced by the U.S. Geological Survey and free for download (https://water.usgs.gov/software/OTIS/). It is beyond the scope of this chapter to discuss model assumptions and limitations in simulating solute BTCs to estimate transient storage parameters. The reader is reminded that models that simulate multiple unknown parameters are subject to equifinality (multiple plausible parameter estimates).

Comparing MTT among different stream reaches can give an indication of the relative importance of transient storage. MTT should be longer if water and the conservative tracer it transports enter slower flow paths. The fraction of MTT due to transient storage, or F_{med}, can be calculated after simulating the BTC using a solute transport model with and without transient storage (Runkel, 2002).

The shape of the BTC also can give you some idea of the transient storage in the experimental reach. A reach with little transient storage will have a nearly rectangular BTC (Fig. 30.5, similar to 0 m). If transient storage is important, the leading edge to peak or plateau concentration will have a rounded shoulder, and the falling limb of the BTC will have a long tail (Fig. 30.5, similar to 100 m). In many streams with transient storage, the BTC tail is characterized by a power law. You can compare BTCs among streams by plotting the tail (concentration vs. time) on $\log_{10}$ scales and compare the slopes of the lines—a steeper slope would indicate transient storage as less important than lines with shallower slopes. It is important to note that such analysis assumes that the stream concentration returns to background. Such assumptions and other aspects of BTC tail analysis are given by Drummond et al. (2012).

30.3.2 Advanced Method: Reactive (Nonconservative) Solute Dynamics

Simultaneously with the conservative solute, a reactive solute may be released to determine nutrient uptake. Either a pulse or a constant rate approach can be used, as described previously (see also Chapter 31). Determine the needed level of nutrient addition with the constant-rate method (above). Make a stock solution of nutrient, calculate the necessary release solution concentration based on the release rate previously determined for chloride, and add the appropriate amount of stock nutrient solution to the release solution. As nutrient uptake is sensitive to concentration, care should be taken to not excessively elevate nutrient concentration. We have found that with good analytical chemistry, it is possible to raise concentration above ambient by about 20 µg/L and estimate uptake parameters. In the case of a pulse release, one could monitor the reactive tracer breakthrough at the lower-most site, collecting samples manually as conductivity increases, and then analyzed with a computer model to estimate uptake parameters (e.g., Runkel, 2007; Lin and Webster, 2012). Alternatively, multiple sampling stations can be monitored and data analyzed (this approach is presented in greater detail in Chapter 31) as described for constant-rate data. Make sure to collect several samples of ambient concentration before the pulse arrives. It is important to note that pulse releases can introduce nutrient concentrations that approach or exceed saturation, especially close to the point of release, in which case sensitivity to model assumptions (i.e., first-order vs. Monod kinetics) is important (see, for example, Covino et al., 2010; Lin and Webster, 2012).

For constant-rate releases, as with the conductivity measurements, samples for nutrient concentration should be taken from the stream before the release and at the plateau of the release. Collect at least three replicate samples at each site. These samples can be taken in any type of clean container. Many researchers use acid-washed high-density polyethylene (HDPE) containers (e.g., Nalgene), whereas others use disposable centrifuge tubes. The samples should be filtered either as they are collected or as soon as possible once the samples are taken to the lab. Methods of sample preservation vary depending on the nutrient you are using, and you should consult a manual such as *Standard Methods for the Examination of Water and Wastewater* (Clesceri et al., 1998). In most cases it is best to keep samples on ice or refrigerated in the dark and analyze samples within 24 h of collection.

Graph normalized nutrient concentration versus distance, and calculate the longitudinal uptake rate (k_W) and uptake length (S_W) (Fig. 30.6). Nutrient concentrations of the samples collected at plateau must be corrected for background levels (C_b) to get the added nutrient level. Then calculate normalized added nutrient concentrations (C_N) by dividing the nutrient concentrations at a specific site (C_x) by the conservative solute (C_c, corrected for background) concentrations at the site:

$$C_N = \frac{(C_x - C_b)}{C_c} \tag{30.19}$$

By doing this you are essentially correcting for decline in nutrient concentration that may result from lateral inflow over the reach. For steady conditions (e.g., at plateau) the solution of Eq. (30.19) is a negative exponential:

$$C_N = C_{N0} e^{-k_W x} \tag{30.20}$$

where C_{N0} = added nutrient concentration at the release site, and x = distance downstream from the release site. Taking the logarithm of both sides of Eq. (30.20) gives:

$$\ln(C_N) = \ln(C_{N0}) - k_W x \tag{30.21}$$

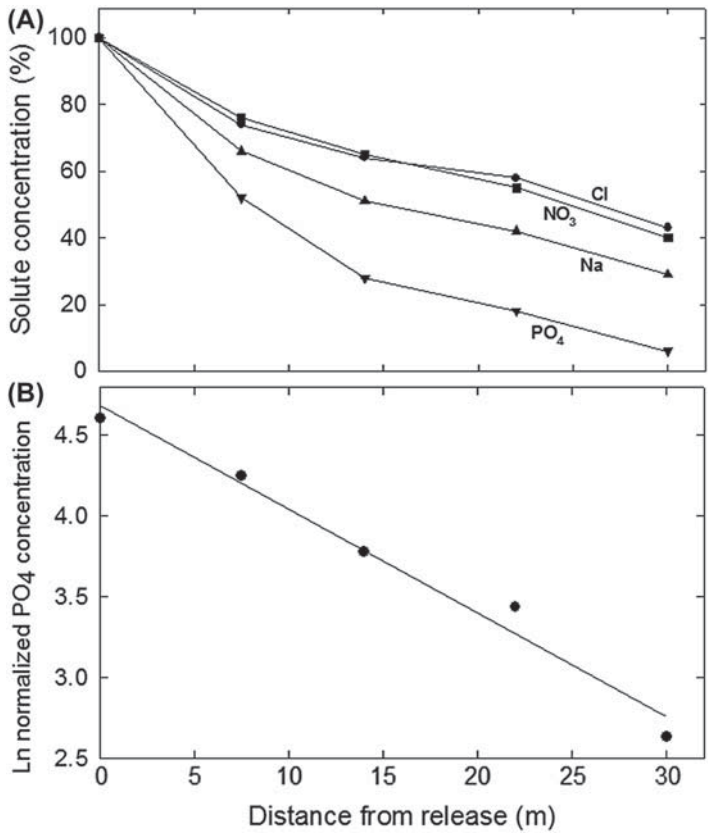

FIGURE 30.6 (A) Plateau concentrations of solutes versus distance expressed as a percent of upstream concentrations. In this stream, NO_3 was relatively abundant and acted like a conservative solute. PO_4 was rapidly removed from the stream water column. (B) Semilog plot of normalized PO_4 concentration versus distance. The slope of this line is the PO_4 longitudinal uptake rate (k_W).

This is the equation for a straight line with intercept of $\ln(C_{N0})$ and a slope of $-k_W$. So, if you use your data to determine a regression of $\ln(C_N)$ versus x, the k_W will be an estimate of the longitudinal uptake rate, and uptake length (S_W) is the inverse of this (Stream Solute Workshop, 1990). Uptake (U) and uptake velocity (v_f) can then be calculated using the metric triad (Fig. 30.2).

30.4 QUESTIONS

1. What are the causes of hydraulic retention (transient storage) in a stream? That is, what causes temporary retention of conservative solutes?
2. Which stream features affect solute retention?
3. If you recovered less mass of conservative tracer than you added, how might this influence your interpretation of the discharge estimate you calculated from your tracer test?
4. Which factors determine the usefulness of various conservative and reactive solute tracers?
5. How does stream size affect hydraulic parameters? Nutrient uptake?
6. What is the significance of wood in streams in terms of solute dynamics? How do you think historical wood removal from streams and rivers might affect solute dynamics?
7. Consider how other human modifications of streams and stream channels may affect solute dynamics. Think about such changes as nutrient enrichment from point and nonpoint sources, dams, channelization, and modification of riparian vegetation.
8. If you conducted conservative and reactive solute tracer tests at multiple plateau concentrations, what was the relationship between areal uptake and concentration?

30.5 MATERIALS AND SUPPLIES

Laboratory materials
- Conservative solute salts
- Reactive solute salts (nutrients)
- Carboys for stock solutions
- Containers for standard solutions (HDPE)
- Deionized or distilled water
- Volumetric flasks (acid washed)

Laboratory equipment
- Analytical instruments for measuring solute concentrations
- Computer with spreadsheet or graphing software
- Analytical balance (±0.001 g or better)
- Filtering apparatus and glass fiber filters

Field materials
- Water-resistant paper or notebook, pencils
- Flagging tape
- Meter stick
- Tape measure (100 m)
- Stopwatches
- Buckets or carboy for solute mixing and delivery
- Graduated cylinder (1000 mL for solute mixing and 10−20 mL for pump calibration)
- Metering pump with tubing and charged batteries
- Sample bottles
- Conductivity meter (with temperature)
- Chloride standard solutions
- Velocity meter and top-setting wading rod or other means to measure stream discharge

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