CHAPTER 8

Solute Dynamics

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I. INTRODUCTION

Solutes are materials that are chemically dissolved in water. This includes 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 the common solutes, which are found in relatively large concentrations in many natural waters, more biologically important solutes such as phosphate and nitrate are normally at very low concentrations. Solutes enter streams from three natural sources. First, the atmosphere (i.e., 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 may also be generated from nitrogen that was biologically fixed by cyanobacteria. Also, inorganic carbon (i.e., CO_2, 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 non-point sources (e.g., agricultural runoff) are often major inputs of solutes to streams.

Solute dynamics refers to the spatial and temporal patterns of solute transport and transformation (Stream Solute Workshop 1990). These processes are tightly coupled to the physical movement of water in all ecosystems, but in streams this coupling is especially important. As materials cycle between biotic and abiotic components of stream ecosystems, they are continuously or periodically transported downstream. Thus the cycles are longitudinally drawn out to form spirals (Webster and Patten 1979, 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 (Peterson *et al.* 2001). Studies of solute dynamics in streams provide two types of information. First, they provide information on the rates of transport and transformation of the solutes themselves, which is important to the

FIGURE 8.1 Field setup for a solute release. This setup was used in a small agricultural stream in North Carolina. The 20-L carboy contained the mixed release solution, and the small table in the stream was used to stabilize the metering pump and battery. The solution was dripped into the center of the stream where the pink ribbon is tied to the hose. Photo by Rob Payn.

understanding of their availability and importance. Second, they can be used to quantify various hydrodynamic properties of a stream. In this chapter, we describe investigations of solute dynamics from both perspectives (Figure 8.1).

Solutes in streams can be classified in various ways (Stream Solute Workshop 1990). Nutrients are those solutes that are essential to the growth, maintenance, and reproduction of some organisms. Nutrients may be limiting to a given process if their concentration is too low to meet biological demand. Other substances such as heavy metals may be inhibitory or toxic to stream organisms. Stream solutes also can be classified according to their biological and chemical reactivity. If their concentration is changed by biotic or abiotic processes, they are referred to as *nonconservative* solutes. On the other hand, if their concentration is not changed by in-stream processes other than dilution, they are called *conservative* solutes. Conservative solutes include things that are not nutrients and do not react chemically with water or the stream substrate, such as lithium or bromide (e.g., Bencala *et al.* 1991). Also, some nonconservative solutes may be so abundant that biotic and abiotic exchanges do not measurably influence stream concentration, and the solute may appear to be conservative and may in fact be treated as a conservative solute. Chloride is an example of a biologically essential solute that exists in most streams in concentrations that far exceed biological need. Thus, chloride is often used as a conservative solute in stream studies (e.g., Triska *et al.* 1989).

A. Conservative Solute Dynamics

The dynamics of conservative solutes in streams are primarily driven by two processes; *advection* and *dispersion*. Advection is downstream movement with the water itself and occurring at the average water velocity. Dispersion can occur by molecular diffusion, but in streams is primarily caused by turbulence. The two processes are expressed in the partial differential equation:

$$\frac{\partial C}{\partial t} = -u\frac{\partial C}{\partial x} + D\frac{\partial^2 C}{\partial x^2} \tag{8.1}$$

where C represents solute concentration; t, time; x, distance in the downstream direction; u, water velocity; and D, dispersion coefficient. However, this equation applies only to conservative solutes in uniform channels with constant discharge. 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 solutes in water that is moving much more slowly than the main body of water (Bencala and Walters 1983), such as water in hyporheic flow paths, pools, and backwaters (Bencala *et al.* 1984, Harvey *et al.* 1996). Including these factors, the equation becomes a pair of equations:

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

and (8.2)

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

where Q is discharge; A, the cross-sectional area of the stream; Q_L, the lateral inflow from groundwater; C_L, the solute concentration of the lateral inflow; α, a coefficient for exchange with the transient storage zones; A_S, the size (expressed as cross-sectional area) of transient storage zones, and C_S, the concentration of solute in the transient storage zone. Other metrics of transient storage can be derived from these parameters (Harvey and Wagner 2000, Runkle 2002). Because discharge (Q) and the cross-sectional area (A) are now changing with stream distance, they must be explicit in the equation.

Despite its apparent complexity, this model, like any model, is a simplification of what is actually occurring in streams. In reality there is probably a whole continuum of transient storage zones rather than a single transient storage compartment; however, this model has been shown to work well in many streams.

B. Dynamics of Nonconservative Solutes

Dynamics of nonconservative solutes are more complicated because of the production and consumption of solutes by in-stream processes. In small streams, the majority of these

processes occur on the stream bottom. They include abiotic processes, such as adsorption, desorption, precipitation, and dissolution. There are also many important biotic processes including heterotrophic (i.e., microbial) uptake, plant uptake, and mineralization. In general, abiotic and biotic processes that remove solutes from the water column are called immobilization. In streams the most important immobilization processes for biologically important solutes (i.e., nutrients) are adsorption (especially for phosphate), heterotrophic uptake, and attached algal uptake. Ignoring the complications we just added in Equation 8.2, the dynamics of a nonconservative solute can be expressed as:

$$\frac{\partial C}{\partial t} = -u\frac{\partial C}{\partial x} + D\frac{\partial^2 C}{\partial x^2} - \lambda_C C \tag{8.3}$$

where C is the nonconservative solute concentration, λ_C is the overall dynamic uptake rate (units of inverse time), and other terms are as defined previously. Of course, nutrients that are immobilized may eventually be mineralized and returned to the water column. This can be most simply expressed by adding another term to Equation 8.3 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 (8.4)

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

where C_B is the immobilized (i.e., benthic) nutrient standing crop (mass per unit area), z is depth, and λ_B is the rate of mineralization.

These equations (or models) of solute dynamics can be much more complicated. This description was adapted from the more complete presentation generated by the Stream Solute Workshop (1990). The very simplest equation (Equation 8.1) can be solved analytically, but the other equations can be solved only by using computers and numerical solution techniques.

As a nutrient atom cycles between inorganic and organic forms, 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 distance traveled in dissolved inorganic form before it is removed from solution, called the uptake length (S_w), and (2) the distance traveled before being mineralized and returned to the water column, called the turnover length (S_B):

$$S = S_W + S_B \tag{8.5}$$

Because much of the organic material in small streams resides on 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 in headwater streams (Newbold *et al.* 1983, Mulholland *et al.* 1985). Accordingly, the focus of this chapter is on the dynamics of dissolved inorganic nutrients as addressed by S_w and related measures.

Mathematically, uptake length can be related back to the previous equations as the inverse of the longitudinal uptake rate:

$$S_W = \frac{1}{k_W} \tag{8.6}$$

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

$$k_W = \frac{\lambda_C}{u} \tag{8.7}$$

Because S_W represents a displacement distance, it is strongly influenced by stream discharge and velocity. To correct for the influence of stream size (i.e., discharge), S_W is often standardized when comparing solute dynamics across systems. This standardization converts S_W to a mass transfer coefficient (Steam Solute Workshop 1990), which describes a theoretical velocity at which a nutrient move towards the location of immobilization (e.g., the stream bed). More recently, the transfer coefficient has been referred to as the uptake velocity (v_f, Peterson *et al.* 2001, Valett *et al.* 2002). The uptake velocity corrects S_W for stream velocity and depth and is calculated as:

$$v_f = \frac{u z}{S_W} \tag{8.8}$$

Coupling v_f and ambient nutrient concentration (C) generates a measure of areal uptake (U):

$$U = v_f C \tag{8.9}$$

Areal uptake (mass per area per time) is a generic descriptor of nutrient cycling similar to measures used in other ecosystems. Uptake refers to the mass of an element taken up (or immobilized) by an area of streambed per unit of time. U reflects the magnitude of the flux of inorganic element from the water column to the biota.

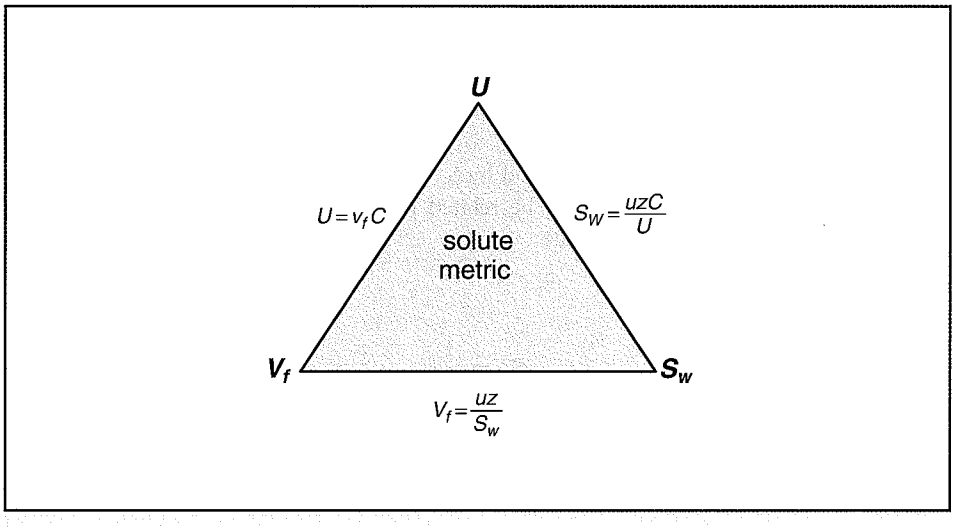

FIGURE 8.2 Metric triad for determining nutrient dynamics in stream ecosystems. Symbols are defined in the text.

Together, these measures (S_W, v_f, and U) form a metric triad of nutrient spiraling (Figure 8.2). Each metric has its utility in the study of nutrient cycling in streams. Areal uptake conveys critical information on biotic consumption but provides no information regarding the spatial aspects of nutrients. Uptake length is a reach or segment scale estimate of retention efficiency and provides explicit information regarding the spatial extent over which nutrient uptake occurs. Uptake velocity standardizes uptake length for discharge (depth and velocity) and provides a more appropriate variable for comparing solute dynamics across streams, although it is strongly influenced by nutrient concentration. Figure 8.2 also illustrates that v_f is a measure of uptake efficiency relative to nutrient availability (Davis and Minshall 1999), which can been seen by rewriting Equation 8.9 as:

$$v_f = \frac{U}{C} \tag{8.10}$$

The objective of the experiments described in this chapter is to examine the dynamics of both a conservative solute and a nonconservative solute (nutrient) in a stream or in a variety of streams. Because of the variability of equipment that might be available and the highly variable nature of stream chemistry, we have provided a number of procedural and experimental options. At a minimum, you should be able to determine discharge, velocity, the importance of transient storage, and an estimate of nutrient uptake. However, the estimate of nutrient uptake we describe here requires elevating the nutrient concentration, which may reduce nutrient uptake relative to supply (e.g., Mulholland *et al.* 2002). Measurement of nutrient uptake not influenced by raising the nutrient concentration above ambient levels requires the use of radioactive (e.g., Newbold *et al.* 1983) or stable (e.g., Peterson *et al.* 2001, Webster *et al.* 2003) isotopes. However, these techniques are time consuming, expensive, and sometimes not permitted. A new method was recently

described by Payn *et al.* (2005), which requires making multiple releases at varying nutrient concentrations. This new method involves significantly more effort, but it should be used if possible. The single nutrient addition method underestimates ambient nutrient uptake, but if used with care it can provide a useful method for comparing nutrient uptake across different sites or under variable experimental conditions.

II. GENERAL DESIGN

The general design of these experiments entails the release of a known concentration of solute at a constant rate into a stream for one to several hours and making measurements downstream to determine the longitudinal pattern of tracer concentration and the timing of the passage of the solute pulse (Figure 8.3).

A. Site Selection

Most solute studies have been done on first- to fourth-order streams that range in discharge from <1 up to 250 L/s. Streams this size allow wadeable access for physical measurements and sampling. Stream flows greater than this may require modification of the release apparatus and sampling design.

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., a straight channel with homogeneous substrate and low amount of wood) and one more complex reach (e.g., sinuous channel, heterogeneous substrate, high amount of wood). Try to avoid reaches with tributary input. Experimental reach length will vary with flow but minimally must be long enough for mixing and dispersion of released solute (a preliminary dye release may be in order). Typical lengths range from 50 m in very small streams to several hundreds of meters in larger systems.

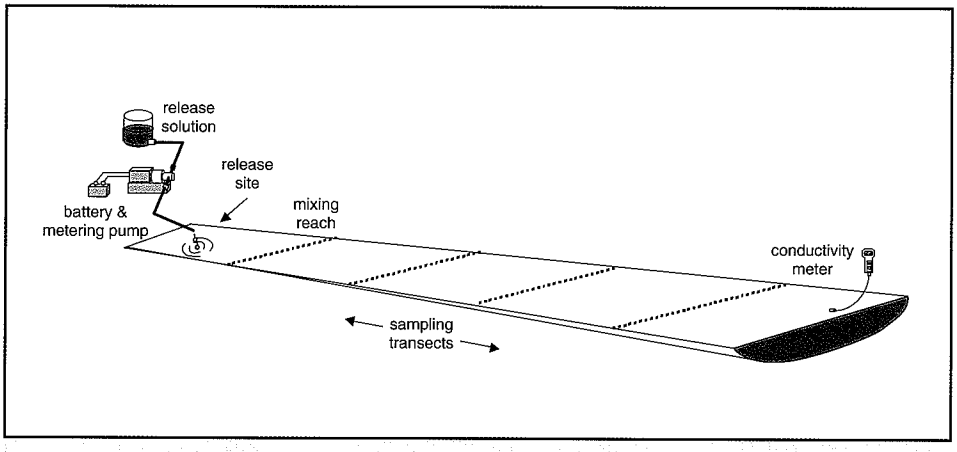

FIGURE 8.3 Diagram of the setup for measuring solute dynamics in a stream.

B. Choice of Solutes

Selection of a conservative solute is a function of local geology, ambient levels of solute in the stream, research budget, and analytical equipment available. It is essential to raise stream concentration of the solute sufficiently above background levels to be analytically detectable. 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 be sure it is noniodized. Most commercial NaCl contains a little cornstarch or other anticaking agents, which will cause a slightly cloudy solution but shouldn't be a problem. Chloride concentration can be measured in several ways. The most convenient way is 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 conductivity meters can be set to automatically adjust to temperature—that is, to measure specific conductance. Portable ion-specific probes are also available for chloride, bromide, sodium, and other ions. Bromide has the advantage of very low background concentrations and can be used in streams where background chloride concentrations are high; however, bromide ion-specific probes are usually less reliable than chloride probes and are influenced by changing chloride concentrations. The disadvantage of sodium is that it loses 5–10% by mass through sorption to stream bottom materials compared to almost no loss of chloride (Bencala 1985). If portable instruments are not available, samples can be collected in the field and analyzed in a laboratory by various spectrographic means.

Selection of a nutrient (nonconservative solute) for study will depend on your knowledge of the streams of interest. You will probably want to use the nutrient that is most limiting to autotrophic and heterotrophic processes, which might be determined with nutrient releasing substrates or experimental nutrient additions (see Chapters 10 and 32). Phosphate and inorganic forms of nitrogen (nitrate or ammonium) are obvious candidates. Your choice may depend on the availability of instrumentation for measuring concentrations of these nutrients. Be sure not to pick a nutrient that precipitates with the conservative solute. For example, calcium and phosphate cannot be used together because they form a highly insoluble salt.

C. Release Techniques

A simple, inexpensive, and nonelectrical release apparatus is the Mariotte bottle (Webster and Ehrman 1996), but battery-powered metering pumps (e.g., Fluid Metering, Inc., Syosset, NY, USA) are generally more reliable and are easily adjusted for variable field conditions.

D. Optional Approaches

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. For each solute release, a computer model can be used to simulate the actual release data and calculate hydraulic parameters such as dispersion and transient storage zone retention. Nonconservative (nutrient) releases can also be run simultaneously with the conservative tracer. A computer simulation of the nonconservative solute dynamics also

may be run and compared with the conservative solute dynamics. Computer simulation methods are described later in this chapter.

E. Data Analysis

Essential physical measurements include discharge, average water depth, and average wetted-channel width for the stream reach over which the release is being conducted. Measurements of other physical parameters such as thalweg velocity, gradient, and "large wood area" or volume are optional. One can calculate hydraulic characteristics (discharge, velocity) from a graph of conservative solute concentration versus time from the results of the experiment; however, it is necessary to have a reasonable estimate of discharge prior to the experiment in order to calculate expected release concentrations. Uptake length and rate can be calculated from nutrient data fit to a negative exponential model. Further hydraulic properties of the reach (i.e., dispersion, transient storage zone area, and exchange rate) can be determined by curve fitting a computer simulation model to the conservative solute data. These techniques are described later in this chapter.

III. SPECIFIC METHODS

A. Basic Method 1: Dynamics of Conservative Solutes

In this example, 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.

Laboratory Preparation

1. Mix stock solution of sodium chloride in 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. Total volume needed depends on the number and duration of releases. Heating the mixture in a water bath aids in dissolution. Mix vigorously and repeatedly to be certain the salt is completely dissolved.
2. Prepare a series of chloride standards (1–20 mg/L) for calibrating the conductivity meter. Calibration involves constructing a standard curve that relates measured specific conductance to chloride concentration across the range of expected chloride concentrations.

Field Prerelease

1. Calculate stream flow and necessary release rate to raise stream concentration measurably above background. We've found that an increase of about 10 μS is generally sufficient if your conductivity meter reads to 0.1 μS. The necessary enrichment for solutes other than conductivity will depend on instrumentation and laboratory capabilities. Discharge can be estimated quickly from cross-sectional area and water velocity (see Chapter 3). The slug-injection method is another easy and

very accurate method of determining stream flow (Gordon *et al.* 2004). Once discharge is known, the release rate (Q_R) can be calculated as:

$$Q_R = \frac{Q * C_S}{C_I} \tag{8.11}$$

where Q is stream discharge; C_S, target stream concentration of added solute; and C_I, the concentration of solute in the release solution. Setting the pump to the calculated release rate will need to be done in the field, and the procedure is described in the next section.

2. Use a tape measure to delimit the extent of the experimental reach. Mark every 5 m (for a 100-m reach) within the reach with labeled flagging tape. At each 5-m transect, measure wetted channel width, depth across the stream (approximately 10 depth 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. Stream temperature and gradient (optional) should also be measured.
3. Calibrate the conductivity meter with the standards. The standards should be placed in the stream until they equilibrate with ambient stream temperature. Alternatively, conductivity (actually specific conductance) itself can be used as the conservative measure. To determine the conductivity of the release solution, make a 1:10,000 dilution (0.1 mL of release solution in 1 L of water) and measure conductivity.

Field Release

1. Make a series of background conductivity measurements in midstream at 10-m intervals (assuming a 100-m reach) along the reach. Work from downstream to upstream and avoid unnecessary disturbance of the study area. Then place the meter securely in a well-mixed area at the downstream site and assign a person to record conductivity during the release.
2. Place the release solution and pump at the upstream site. Check the pump rate with a graduated cylinder and stopwatch and adjust as necessary to the calculated release rate. Keep a bucket under the release hose to avoid any premature addition to the stream. During the release, periodically check and record the release rate, emptying collected solute in the graduated cylinder into the stream.
3. Be sure the release solution is stable and covered. Also, check the hoses to be sure they are secure and not laying in the stream.
4. Synchronize stopwatches and begin the release. The frequency of readings at the downstream site depends upon the rate at which the concentration changes in the stream. Record conductivity readings every 1–5 min (flow dependent) until pulse arrives and then every 15–30 s as chloride concentration increases rapidly.
5. At plateau, that is, when the conductivity is no longer changing (30 min to several hours after commencing release), working from downstream to upstream, again take measurements of conductivity 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 and shut off the release. Record the total time of release (i.e., the duration of the solute addition).

6. Continue recording downstream conductivity until stream levels return to near prerelease levels. We have frequently found that conductivity readings never return to background levels, either because of actual change in background or drift in the conductivity meter. To correct for either of these problems, it is useful to measure conductivity above the release site several times during the study.

Data Analysis

1. Summarize physical parameters: mean width and mean depth at each cross section and over the whole reach, mean velocity (optional), and gradient (optional).
2. Graph conservative solute concentrations versus time at the downstream end of the reach (Figures 8.4 and 8.5).
3. From this graph calculate discharge, Q, from plateau concentrations:

$$Q = \frac{(C_R - C_b) * Q_R}{C_p - C_b} \tag{8.12}$$

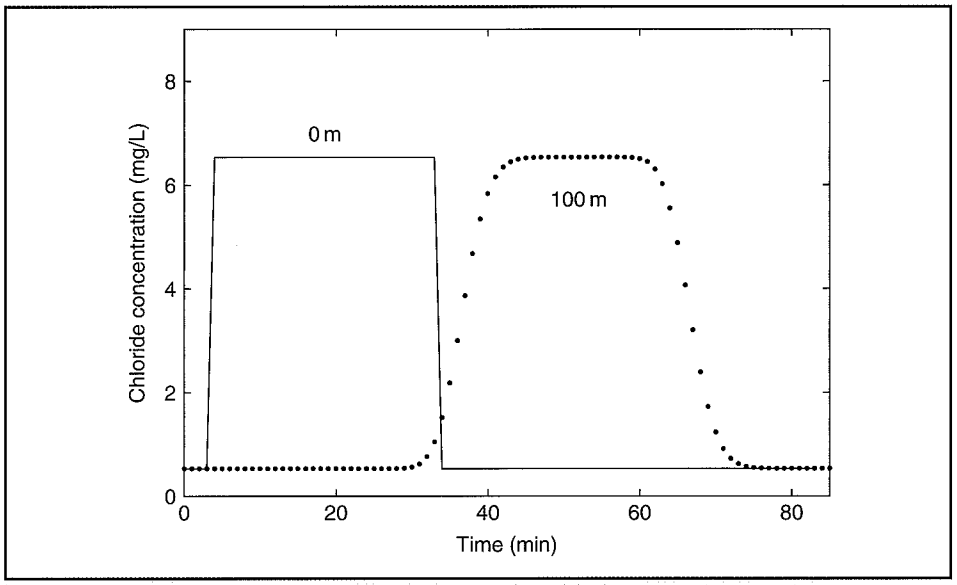

FIGURE 8.4 Chloride concentration versus time for a small stream with very little transient storage and no increase in flow over the reach.

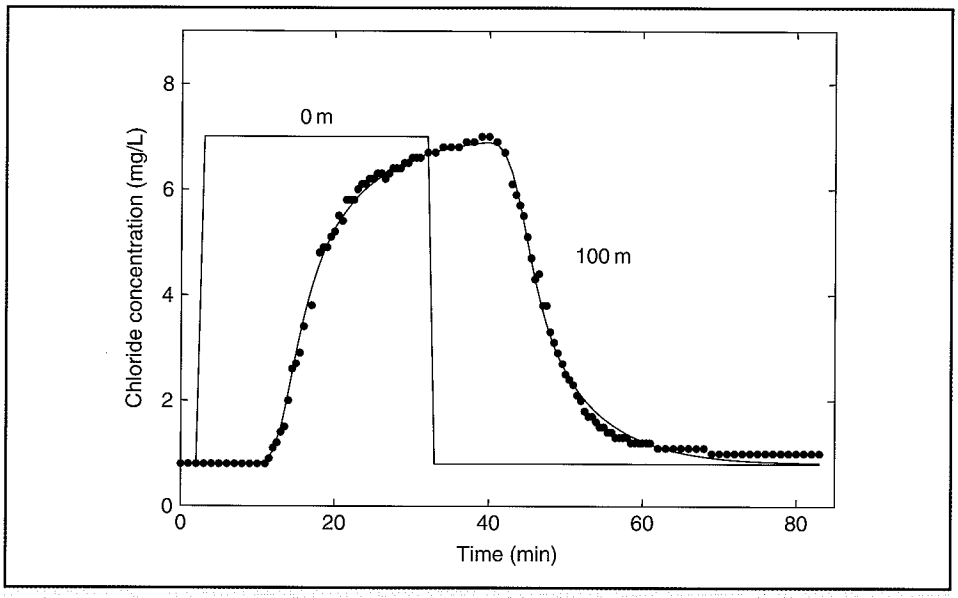

FIGURE 8.5 Chloride concentration versus time for a stream with considerable transient storage and no increase in flow over the reach. At 100 m the dots are actual data and the solid line is a computer simulation of these data using a transient storage model.

where Q_R is release rate; C_R, the chloride (or conductivity) concentration of the release solution; C_P, the plateau chloride concentration; and C_b, background (i.e., prerelease) chloride concentration. Compare this measurement of discharge with direct measurements. If conductivity is used, C_R can be calculated as 10,000 times the conductivity of a 1:10,000 dilution of the release solution.

4. A useful measure of hydraulic retention is the median travel time (MTT), which is the time required for 50% of the chloride to pass out of the stream reach (Runkel 2002). This can be determined by integration of the chloride curve (which can be done with many graphics or spreadsheet programs). Dividing the length of the reach by MTT gives the average solute velocity, which can be compared with direct measurements of thalweg velocity. For example, in Figure 8.4 the chloride release began at 12:04 and lasted 30 minutes. One hundred meters downstream, the solute pulse came by between 12:30 and 1:10. By integrating the curve, we determined that half of the added solute had passed by the 100-m point by 12:55. Since one-half of the 30-min release was completed by 12:19, MTT was 36 minutes (12:55-12:19). One hundred meters divided by 36 minutes is 4.6 cm/s.
5. Similarly, you can calculate discharge at points along the reach by using the plateau concentrations (Figure 8.6). Graph discharge versus distance to see if there is evidence of groundwater input. If there is evidence of flow increase at a specific point (or points), go back to the stream and see if you can identify landscape features associated with this subsurface input.
6. Comparison of your data to the curves in Figure 8.4 and 8.5 should give you some idea of the transient storage in your experimental reach. A reach with little or no transient storage will have a nearly rectangular graph (Figure 8.4). If transient

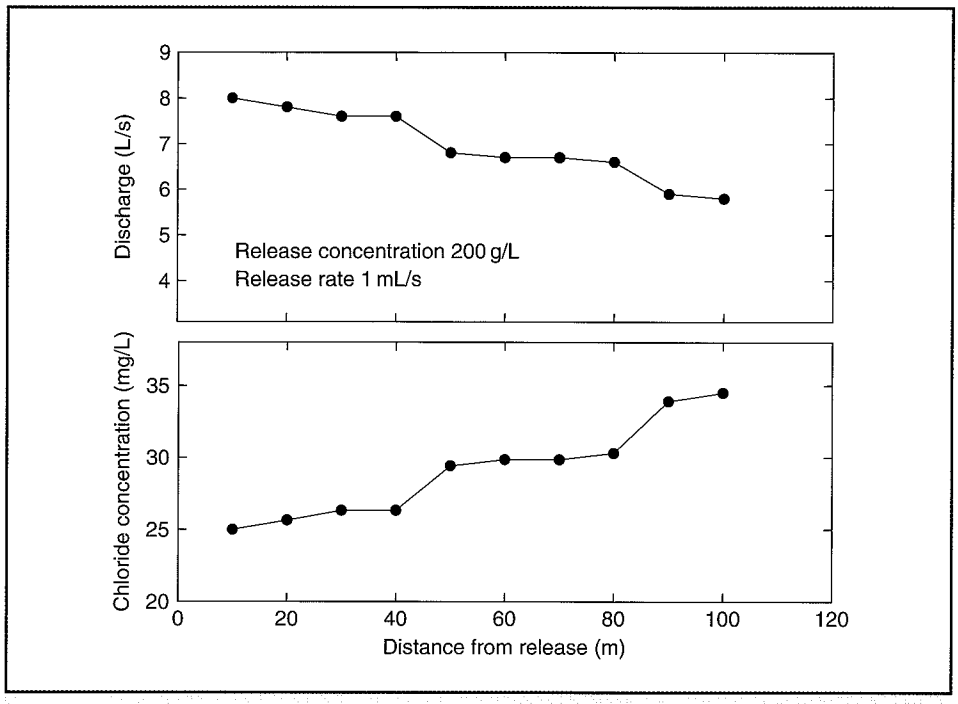

FIGURE 8.6 Plateau concentrations of chloride versus distance (top) and calculated discharge versus distance (bottom) for a stream with significant groundwater input over the reach.

storage is large, the uptake arm of the curve will have a rounded shoulder and the falling side of the graph will have a long tail (Figure 8.5).

B. Basic Method 2: Dynamics of Nonconservative Solutes

Simultaneously with the conservative solute, a nonconservative solute may be released to determine nutrient uptake. Determine the needed level of nutrient addition. 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. You will need to calculate your actual release chloride concentration as a result of dilution with the nutrient stock solution. 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. If you are using glassware, acid washing will be necessary. We 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 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 and analyze samples within 24 h of collection.

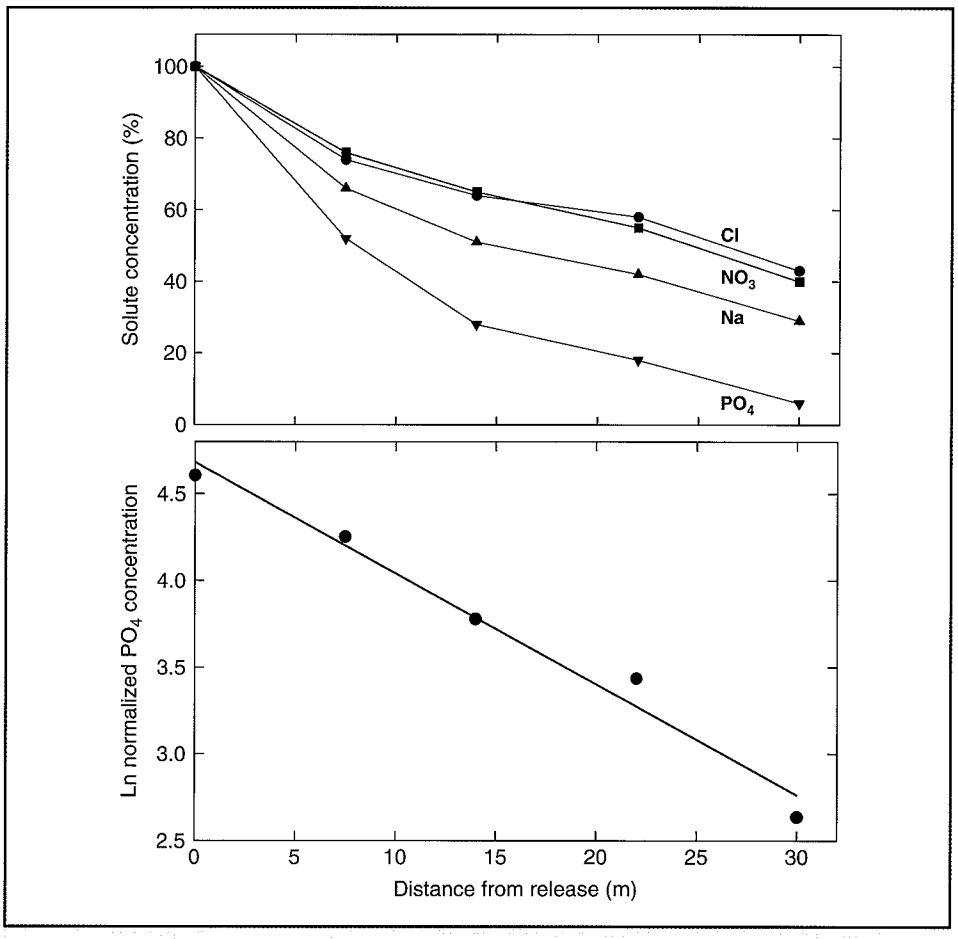

FIGURE 8.7 (Top) Plateau concentrations of solutes versus distance expressed as a percent of upstream concentrations. In this stream NO_3 was relatively abundant and acted like a conservative solute. PO_4 was rapidly taken up from the stream. (Bottom) Semi-log plot of normalized PO_4 concentration versus distance. The slope of this line is the PO_4 longitudinal uptake rate (k_L).

Graph normalized nutrient concentration versus distance and calculate the longitudinal uptake rate (k_W) and uptake length (S_W) (Figure 8.7). Nutrient concentrations of the samples collected at plateau must be corrected for background levels (C_b) in order 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:

$$C_N = \frac{(C_x - C_b)}{C_c} \tag{8.13}$$

By doing this you are essentially correcting for decline in nutrient concentration that may result from in-flow over the reach. For steady conditions (e.g., at plateau) the solution of Equation 8.3 is a negative exponential:

$$C_N = C_{N0} e^{-k_W x} \tag{8.14}$$

where C_{N0} is the added nutrient concentration at the release site, and x is distance downstream from the release site. Taking the logarithm of both sides of Equation 8.14 gives:

$$\ln(C_N) = \ln(C_{N0}) - k_W x \tag{8.15}$$

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 slope (k_W) will be an estimate of the longitudinal uptake rate, and uptake length (S_w) is the negative inverse of this (Stream Solute Workshop 1990). Uptake (U) and uptake velocity (v_f) can then be calculated using the metric triad (Figure 8.2).

C. Advanced Method 1: Computer Simulation

There are various computer models that can be used to simulate the results of your experiment (Figure 8.5). One example is a program called OTIS (One-dimensional Transport with Inflow and Storage), which is available on the web (http://webserver.cr.usgs.gov/otis). This simulation program was written by Robert L. Runkel, U.S. Geological Survey, Denver Federal Center, Denver, Colorado 80225, USA. It can be used to calculate transient storage parameters from the results of a conservative solute release experiment (Runkel 1998).

IV. QUESTIONS

1. What are causes of hydraulic retention in a stream? (That is, what causes temporary retention of conservative solutes?)
2. What stream features affect retention of solutes?
3. What factors determine the usefulness of various conservative and nonconservative solutes?
4. How does stream size affect hydraulic parameters?
5. What is the significance of wood in streams in terms of solute dynamics? How do you think the historical removal of wood from streams and rivers has affected solute dynamics?
6. Consider how various human modifications of streams and stream channels may affect solute dynamics. Think about such changes as nutrient enrichment from point sources or non-point runoff, channalization, dam construction or dam removal, and modification of riparian vegetation.

V. MATERIALS AND SUPPLIES

Laboratory Materials

Conservative solute
Nonconservative solute (nutrient)
Carboy for stock solution of solutes
Containers for standards
Distilled water
Graduated cylinders (100 mL and 1000 mL)

Lab Equipment

Analytical instruments (for measuring solute concentrations)
Computer (optional)
Electronic balance (±0.01 g)
Filtering apparatus and filters

Field Materials

Water-resistant paper or notebook, pencils
Flagging tape
Permanent marking pen
Meter stick
Tape measure (50–100 m)
Stopwatches
Thermometer
Bucket
Graduated cylinder (100 mL)
Metering pump with tubing, battery
Sample bottles
Conductivity meter
Chloride standards
Velocity meter (optional)

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VII. REFERENCES

Bencala, K. E. 1985. Performance of sodium as a transport tracer: experimental and simulation analysis. *Water Supply Paper* 2270:83–89, United States Geological Survey, Reston, Virginia.

Bencala, K. E., V. C. Kennedy, G. W. Zellweger, A. P. Jackman, and R. J. Avanzino. 1984. Interactions of solutes and streambed sediment 1. An experimental analysis of cation and anion transport in a mountain stream. *Water Resources Research* 20:1797–1803.

Bencala, K. E., B. A. Kimball, and D. M. McKnight. 1991. Use of variation in solute concentration to identify interactions of the substream zone with instream transport. Pages 377–379 *in* G. E. Mallard and

D. A. Aronson (Eds.) *U.S. Geological Survey Toxic Substances Hydrology Program, Water-Resources Investigations Report* 91-4034. U.S. Geological Survey, Reston, VA.

Bencala, K. E., and R. A. Walters. 1983. Simulation of solute transport in a mountain pool-and-riffle stream: a transient storage model. *Water Resources Research* **19**:718–724

Clesceri, L. S., A. E. Greenberg, and A. D. Eaton. 1998. *Standard Methods for the Examination of Water and Wastewater*, 20th ed. American Public Health Association, Washington, DC.

Davis, J. C., and G. W. Minshall. 1999. Nitrogen and phosphorus uptake in two Idaho (USA) headwater wilderness streams. *Oecologia* 119:247–255.

Elwood, J. W., J. D. Newbold, R. V. O'Neill, and W. VanWinkle. 1983. Resource spiraling: an operational paradigm for analyzing lotic ecosystems. Pages 3–27 *in* T. D. Fontain III and S. M. Bartell (Eds.) *Dynamics of Lotic Ecosystems*. Ann Arbor Science, Ann Arbor, MI.

Fisher, S. G., and G. E. Likens. 1973. Energy flow in Bear Brook, New Hampshire: an integrative approach to stream ecosystem metabolism. *Ecological Monographs* **43**:421–439.

Gordon, N. D., T. A. McMahon, B. L. Finlayson, C. J. Gippel, and R. J. Nathan. 2004. *Stream Hydrology: An Introduction for Ecologists*. Wiley, Chichester, UK.

Harvey, J. W., and B. J. Wagner. 2000. Quantifying hydrologic interactions between streams and their subsurface hyporheic zones. Pages 3–44 *in* J. B. Jones and P. J. Mulholland (Eds.) *Streams and Ground Waters*. Academic Press, San Diego, CA.

Harvey, J. W., B. J. Wagner, and K. E. Bencala. 1996. Evaluating the reliability of the stream tracer approach to characterize stream-subsurface water exchange. *Water Resources Research* 32:2441–2451.

Minshall, G. W., S. A. Thomas, J. D. Newbold, M. T. Monaghan, and C. E. Cushing. 2000. Physical factors influencing fine organic particle transport and deposition in streams. *Journal of the North American Benthological Society* **19**:1–16.

Mulholland, P. J., J. W. Elwood, J. D. Newbold, and L. A. Ferren. 1985. Effect of a leaf-shredding invertebrate on organic matter dynamics and phosphorus spiralling in heterotrophic laboratory streams. *Oecologia* 66:199–206.

Mulholland, P. J., A. D. Steinman, E. R. Marzolf, D. R. Hart, and D. L DeAngelis. 1994. Effect of periphyton biomass on hydraulic characteristics and nutrient cycling in streams. *Oecologia* **98**:40–47.

Newbold, J. D., J. W. Elwood, R. V. O'Neill, and W. VanWinkle. 1981. Measuring nutrient spiralling in streams. *Canadian Journal of Fisheries and Aquatic Sciences* **38**:860–863.

Newbold, J. D. 1992. Cycles and spirals of nutrients. Pages 370–408 *in* P. Calow and G. E. Petts (Eds.) *The Rivers Handbook*. Blackwell Scientific, Oxford, UK.

Newbold, J. D., J. W. Elwood, R. V. O'Neill, and A. L. Sheldon. 1983. Phosphorus dynamics in a woodland stream ecosystem: a study of nutrient spiraling. *Ecology* **64**:1249–1265.

Payn, R. P., J. R. Webster, P. J. Mulholland, H. M. Valett, and W. K. Dodds. 2005. Estimation of stream nutrient uptake from nutrient addition experiments. *Limnology and Oceanography: Methods* 3:174–182.

Peterson, B. J., W. Wollheim, P. J. Mulholland, J. R. Webster, J. L. Meyer, J. L. Tank, E. Martí, W. B. Bowden, H. M. Valett, A. E. Hershey, W. H. McDowell, W. K. Dodds, S. K. Hamilton, S. V. Gregory, and D. D. Morrall. 2001. Control of nitrogen export from watersheds by headwater streams. *Science* **292**:86–90.

Runkel, R. 1998. One-dimensional transport with inflow and storage (OTIS): a solute transport model for streams and rivers. *Water-Resources Investigations Report* 98-4018, U.S. Geological Survey, Denver, CO.

Runkel, R. 2002. A new metric for determining the importance of transient storage. *Journal of the North American Benthological Society* **21**:529–543.

Stream Solute Workshop. 1990. Concepts and methods for assessing solute dynamics in stream ecosystems. *Journal of the North American Benthological Society*. **9**:95–119.

Triska, F. J., V. C. Kennedy, R. J Avanzio, G. W. Zellweger, and K. E. Bencala. 1989. Retention and transport of nutrients in a third-order stream in northwestern California: Hyporheic processes. *Ecology* 70:1893–1905.

Valett, H. M., C. L. Crenshaw, and P. F. Wagner. 2002. Stream nutrient uptake, forest succession, and biogeochemical theory. *Ecology* **83**:2888–2901.

Webb, B. W., and D. E. Walling. 1992. Water quality. Chemical characteristics. Pages 73–100 *in* P. Calow and G.E. Petts (Eds.) *The Rivers Handbook*. Blackwell Scientific, Oxford, UK.

Webster, J. R., and B. C. Patten. 1979. Effects of watershed perturbation on stream potassium and calcium dynamics. *Ecological Monographs* **49**:51–72.

Webster, J. R., and T. P. Ehrman. 1996. Solute dynamics. Pages 145–160 *in* F. R. Hauer and G. A. Lamberti (Eds.) *Methods in Stream Ecology*. Academic Press, San Diego, CA.

Webster, J. R., P. J. Mulholland, J. L. Tank, B. J. Peterson, W. R. Dodds, H. M. Valett, W. B. Bowden, C. N. Dahm, S. Findlay, S. V. Gregory, N. B. Grimm, S. K. Hamilton, S. L. Johnson, E. Martí, W. B. McDowell, J. L. Merriam, D. D. Morrall, J. L. Meyer, S. A. Thomas, and W. M. Wollheim. 2003. Factors affecting ammonium uptake in streams — an inter-biome perspective. *Freshwater Biology* 48:1329–1352.