CHAPTER 8

Solute Dynamics

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I. INTRODUCTION

The term *solute* is used for materials that are chemically dissolved in water. This includes materials such as calcium, chloride, sodium, potassium, magnesium, silica, and carbonate, which are often in relatively large concentrations. More biologically important solutes such as phosphate and nitrate are normally at very low concentrations. These solutes enter streams from three natural sources (e.g., Webb and Walling 1992). 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, nitrate may enter from the atmosphere or from weathering, or it may also come from biological fixation by blue-green algae. Also, inorganic carbon (CO_2, bicarbonate, or carbonate) comes from the atmosphere, weathering, or respiration by soil and stream organisms. Point (i.e., pipes) and nonpoint (e.g., agricultural runoff) are often major sources of solutes.

Solute dynamics refers to the spatial and temporal patterns of solute transport and transfer (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 the materials cycle

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between biotic and abiotic components of the stream ecosystem, they are continuously or periodically transported downstream. Thus the cycles are longitudinally drawn out in 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. 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 understanding of the availability (or impact) of the solutes. Second, they can be used to quantify various hydrologic properties of a stream. In this chapter, we will investigate solute dynamics from both perspectives.

Solutes in streams can be classified in various ways (Stream Solute Workshop 1990). Nutrients are those solutes that are essential to the growth and reproduction of some organisms. Nutrients may be limiting 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.* On the other hand, if their concentration is not changed by in-stream processes, 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 (e.g., Bencala *et al.* 1991). Also, some nutrients may be so abundant that biotic and abiotic exchanges are very small relative to the 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. Chloride is often used as a conservative solute in stream studies (e.g., Triska *et al.* 1989).

The dynamics of a conservative solute are primarily driven by two processes; *advection* and *dispersion.* Advection is the downstream transport at the 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

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

where C represents solute concentration; t, time; x, distance in the downstream direction; u, water velocity; and D, a 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 and tributary inputs, and transient storage. *Transient storage* refers to the temporary storage of solutes in water that is moving more slowly than the main body of water, such as pools, backwaters, and hyporheic water (Bencala and Walters 1983). Including these factors, the equation becomes:

$$\frac{\partial C}{\partial t} = \frac{-Q}{A}\frac{\partial C}{\partial x} + \frac{1}{A}\frac{\partial}{\partial x}\left[\frac{AD\partial C}{\partial x}\right] + \frac{Q_L}{A}(C_L - C) + \alpha(C_S - C) \quad (8.2)$$

and

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

where Q is discharge; A, the cross-sectional area of the stream; Q_L, the lateral inflow from groundwater or tributaries; C_L, the solute concentration of the lateral inflow; α, a coefficient for exchange with the transient storage zones; A_S, the size of the transient storage zones, and C_S, the concentration of solute in the transient storage zone.

Dynamics of nonconservative solutes are more complicated because of the exchanges between solute in the water column and on the stream substrate. These exchanges include abiotic processes, such as adsorption, desorption, precipitation, and dissolution. There are also many important biotic exchanges. Examples of biotic exchanges include heterotrophic (i.e., microbial) uptake, plant uptake, leaching, and mineralization. In general, abiotic or biotic process 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 plant uptake. Ignoring the complications we just added in Eq. (8.2), the dynamics of a nonconservative solute can be expressed as

$$\frac{\partial C}{\partial t} = -u\frac{\partial C}{\partial x} + D\frac{\partial^2 C}{\partial x^2} - k_C C, \quad (8.3)$$

where k_C is the overall uptake rate. Of course, nutrients that are immobilized may eventually be returned to the water column. This can be most simply expressed by adding another term to Eq. (8.3) and adding another equation for the immobilized nutrient,

$$\frac{\partial C}{\partial t} = -u\frac{\partial C}{\partial x} + D\frac{\partial^2 C}{\partial x^2} - k_C C + \frac{1}{h}k_B C_B \tag{8.4}$$

and

$$\frac{\partial C_B}{\partial t} = hk_C C - k_B C_B,$$

where C_B is the immobilized (i.e., benthic) nutrient concentration and k_B is the rate of remobilization.

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

As noted above, nutrients cycle (in the standard ecological sense) between abiotic and biotic forms, but in streams this cycling is constantly subject to downstream displacement, resulting in a pattern described as *spiralling*. Another way of looking at nutrient dynamics (i.e., the dynamics of nonconservative, biologically important solutes) is in terms of *spiralling length;* the distance a nutrient atom travels while completing a cycle (i.e., while going from abiotic form to biotic and back to abiotic (e.g., Elwood *et al.* 1983, Newbold 1992)). Spiralling length has two components: (1) the distance traveled while in abiotic form (dissolved in the water column) before being immobilized, called the *uptake length,* and (2) the distance traveled before being remobilized and returned to the water column, called the *turnover length.* Thus,

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

where S represents spiralling length; S_W, uptake length; and S_B, turnover length. Uptake length can be related back to the previous equations because it is the inverse of the uptake rate:

$$S_W = 1/k_C. \tag{8.6}$$

As we will see in this chapter, uptake length can be determined with fairly simple experimental techniques. However, determination of turnover length is much more difficult and has been done only using radioactive tracers (e.g., Newbold *et al.* 1983). In most cases uptake length is the major

component of spiralling length. When a nutrient atom is dissolved in the water column it is free to travel with the water (i.e., it is mobile), but after it is immobilized it is attached to or part of a particle and its downstream velocity is much slower.

The objective of the experiments described in this chapter is to examine the dynamics of both a conservative solute and a nonconservative solute 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, and the importance of transient storage.

II. GENERAL DESIGN

The general design of these experiments is that a known concentration of solute is released at a constant rate into a stream for one to several hours. Measurements are made downstream to determine the concentration and timing of the passage of the solute pulse.

A. Site Selection

Most solute studies have been done on first- to fourth-order streams that range in discharge from <1 up to 250 liters/s. Streams this size allow wadeable access for physical measurements and sampling. Stream flows greater than this may require scaling up of the release apparatus and modification of sampling design and execution. It may be necessary to calculate discharge prior to the experiment either with a "quick and dirty" dye release or with physical measurements (see Chapter 3).

Choice of a stream or section of stream will depend on the question posed (e.g., single reach or comparison of multiple reaches—see options). 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 should encompass 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. The length of experimental reaches 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 fairly small streams to several hundred meters in larger streams.

B. Choice of Solutes

Selection of a conservative solute tracer is a function of local geology, ambient levels of solute in the stream, research budget, and analytical equipment available. It is desirable to raise stream concentration of the solute 5- to 10-fold over background levels. Typical conservative solutes used are salts of Cl, Na, Li, K, and Mg. Of these, Cl, either as NaCl or LiCl, is the most common. Cl can easily be obtained as NaCl (available at the local grocery store—make sure it is noniodized) and can be measured several ways. The most convenient way is with a portable ion-specific probe, which eliminates any laboratory analysis. Sodium-specific probes are also available, but sodium loses 5–10% by mass through sorption to stream bottom materials compared to almost no loss of chloride (Bencala 1985). Salt concentration also can be measured with a high-quality conductivity meter (e.g., Mulholland *et al.* 1994). If portable instruments are not available, samples can be collected in the field and analyzed in a laboratory by various spectrographic means.

C. Mariotte Bottle

A simple, inexpensive, reliable, and nonelectrical release apparatus is the Mariotte bottle (Fig. 8.1). Named for its 17th century creator, Edme Mariotte, the "bottle" allows for delivery of solute solution at a constant release rate, despite the change in head of the reservoir. Its parts include only a carboy with volume of approximately 12 liters sealed at the top with a rubber stopper. A rigid plastic tube extends through a hole in the stopper to just above the bottom of the carboy. As long as the tube remains below the liquid level, the solution drains at a constant rate through a spigot at the bottom. Calibrated tips (50-μl automatic pipet tips) connected to the spigot by rubber tubing allow variable release rates. In the lab, one can calibrate tips cut to various aperture sizes to obtain various delivery rates. The delivery rate can also be adjusted by connecting the tip to the carboy spigot with flexible tubing and changing the height of the dispensing tip. Release rate may fluctuate with changes in barometric pressure or elevation.

D. Optional Exercises

Several optional experiments are presented in this chapter. Beyond the single reach release, solute dynamics can be compared spatially among the reaches of one to several streams, before and after a 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

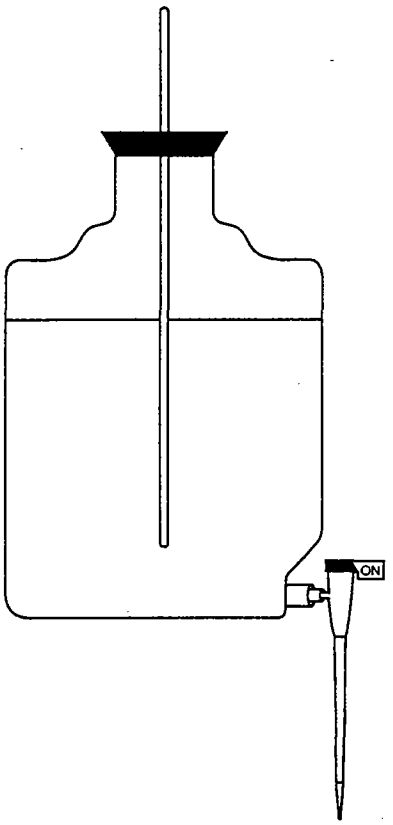

FIGURE 8.1 Mariotte bottle.

conservative tracer. A computer simulation of the nonconservative solute dynamics also can be run and uptake length calculated.

E. Data Analysis

Necessary 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 thalweg velocity, gradient, and large woody debris area or volume are optional. One can calculate hydraulic characteristics (discharge, nominal transport time (NTT)) from a graph of conservative solute concentration versus time, and uptake length and rate can be calculated from nutrient data fit to a negative exponential model. Further hydraulic properties of the reach (dispersion, transient

storage zone area and exchange rate) can be determined by subjective curve fitting of a computer simulation model to the conservative solute data. These techniques are described below.

III. SPECIFIC EXERCISES

A. Exercise 1: Dynamics of a Conservative Solute

Laboratory Preparation

1. Mix stock solution of sodium chloride (238 g/liter) in distilled water. Total volume needed depends on the number of releases, duration of release, and release rate. Heating the mixture in a water bath aids in dissolution. Mix vigorously and repeatedly for the solution is close to saturation. Make certain the salt is completely dissolved.
2. Prepare a series of chloride standards (1–20 mg/liter) for calibrating the probe.
3. Calibrate several pipet tips for the Mariotte bottle to cover a broad span of possible release rates.

Field Prerelease

1. Calculate stream flow and necessary release rate to raise stream concentration 5–10 fold that of background. Discharge can be estimated quickly from cross-sectional area and water velocity (determined by timing a buoyant piece of material floating down a measured reach) or with a dye release (see Chapters 3 and 11). Release rate (Q_I) is calculated as

$$Q_I = Q \times C_S/C_I, \tag{8.7}$$

where Q is discharge; C_S, target stream concentration of solute; and C_I, the concentration of solute in the release solution (238 g/liter). Select a tip to deliver solute at this rate.

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.
3. At each 5-m cross section, measure wetted channel width, depth across the stream (every 0.5 m), and thalweg velocity (optional). Stream temperature and gradient (optional) should also be measured.
4. Calibrate the Cl probe with the standards. The standards should be placed in the stream until they equilibrate with ambient stream temperature.

Field Release

1. Collect a series of background water samples in mid-stream at 10-m intervals over the reach. Take three replicates at each site. These samples can be taken in any type of clean container. We use disposable urine cups. Work from downstream up and avoid unnecessary stomping in the stream.

2. Position chloride probe and recorders at the downstream site. Place probe securely in a well-mixed area.

3. Add solute solution to Mariotte bottle and seal with rubber stopper. Position the Mariotte bottle on a stand directly in the stream (if shallow and stable enough) or on bank (with sufficiently long tubing to reach stream) such that the solution will enter a turbulent, well-mixed zone. Do not attach tip to Mariotte bottle at this time.

4. With a bucket under the spigot, open to full and allow Mariotte bottle to equilibrate; you will hear a glug-glug-glug sound as air comes down through the tube. Turn off spigot. Do not break the seal at top or this step will have to be repeated.

5. Connect tubing with appropriate tip. Place bucket under tip and open to flush out any air bubbles. Measure the release rate with a graduated cylinder and stopwatch. Keep the bucket under the tip to avoid any premature addition to the stream. If the release rate is unacceptably higher or lower than expected, a new tip should be used. During the release, periodically recheck the release rate, emptying solute in the graduated cylinder into the stream. (Caution: do not do this prior to the release, rather empty the graduated cylinder into the bucket.)

6. Synchronize stopwatches and open spigot to commence release.

7. Frequency of chloride readings at downstream site depends upon rate at which the concentration changes in the stream. Record probe readings every 1–5 min (flow dependent) until pulse arrives and then measure every 15–30 s as chloride concentration increases rapidly.

8. At plateau (10 min to several hours after commencing release), working from downstream to upstream, take three samples from mid-stream at 10-m intervals (see step 1 above). Again, avoid unnecessary stomping in the stream. Shut off the Mariotte bottle once samples have been collected from all sites. Record the total time of release.

9. Continue recording chloride concentration until stream levels return to prerelease levels. Once measurement in the stream has been terminated, use the probe to measure chloride concentrations of the background and plateau samples. Recalibrate probe, for it may experience electronic drift during the release.

10. If no probe is available, water samples at the downstream site

should be taken before the release and every 1–5 min throughout the release. The volume of sample taken will depend on the laboratory method of measuring solute concentration.

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 concentration versus time at the downstream end of the reach (Fig. 8.2).

3. From this graph calculate discharge, Q, from plateau concentrations,

$$Q = (C_I - C_b) \times Q_I/(C_p - C_b), \tag{8.8}$$

where Q_I is release rate; C_I, the solute concentration of the release solution; C_p, the plateau solute concentration; and C_b, background (i.e., prerelease) concentration. Compare this measurement of discharge with direct measurements.

4. A useful measure of hydraulic retention is the nominal transport time (NTT), which is the time required for 50% of the chloride (or other conservative solute) to pass out of the stream reach (Triska *et al.* 1989). This can be determined by integration of the chloride curve (digitizer or computer approximation). Dividing the length of the reach by NTT gives the average stream velocity, which can be compared with direct measure-

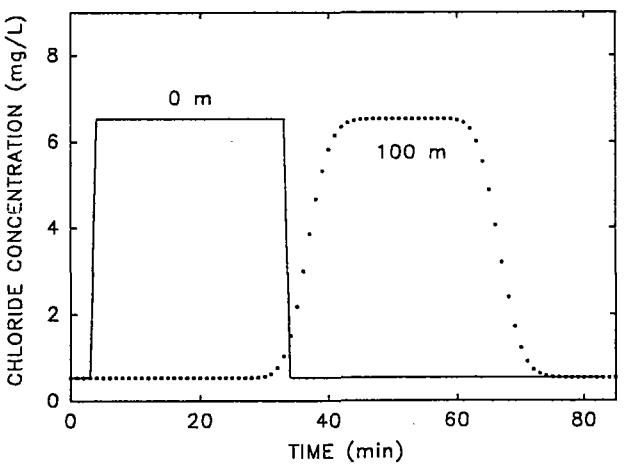

FIGURE 8.2 Chloride concentration versus time for a small stream with very little transient storage and no increase in flow over the reach.

ments of thalweg velocity. For example, in Fig. 8.2 the solute release began at 12:04 and lasted 30 min. One hundred meters downstream, the solute pulse came by between 12:10 and 1:10. By integrating the curve, we determined that half of the added solute had passed the 100-m point by 12:35. Since one-half of the 30-min release was completed by 12:19, NTT was 16 min (12:35 to 12:19). One hundred meters divided by 16 min is 10.4 cm/s. (This example was for a very small stream with a very low gradient.)

5. Similarly, you can calculate discharge along the reach by using the plateau concentrations (Fig. 8.3). 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 Figs. 8.2 and 8.4 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 (Fig. 8.2). If there is lots of transient storage, the uptake arm of the curve will be sloped, instead of a plateau there will be a period of slowly rising concentration, and the falling side of the graph will have a long tail (Fig. 8.4).

B. Exercise 2: Dynamics of a Nonconservative Solute

Simultaneously with the conservative solute, a nonconservative solute may be released to determine nutrient uptake. Samples should be taken

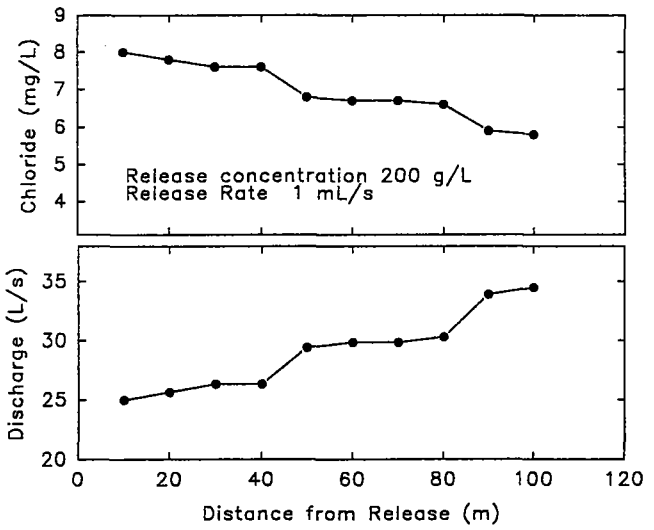

FIGURE 8.3 Plateau concentrations versus distance and calculated discharge versus distance for a stream with significant groundwater input over the reach.

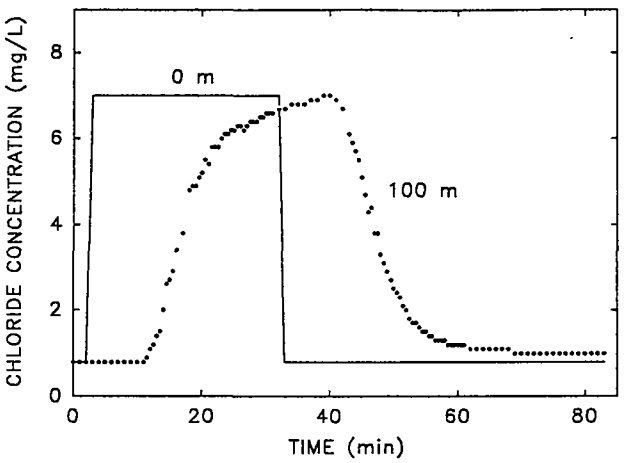

FIGURE 8.4 Chloride concentration versus time for a stream with considerable transient storage.

before the release and at the plateau of the release as with the chloride samples. Choice of appropriate nutrient depends upon local geology and which nutrient is possibly limiting in the stream. 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.

Graph normalized nonconservative solute (nutrient) concentration versus distance and calculate uptake rate (k_C) and uptake length (S_W) (Fig. 8.5). 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 concentrations (C_N) by dividing the nutrient concentrations at a specific site (C_t) by the conservative solute (C_0, corrected for background) concentrations at the site:

$$C_N = (C_t - C_b)/C_0. \tag{8.9}$$

By doing this you avoid the necessity of correcting for possible increase in flow over the reach. For steady conditions (e.g., at plateau) the solution of Eq. (3) is a negative exponential,

$$C_N = C_{N0}e^{-k_C x}, \tag{8.10}$$

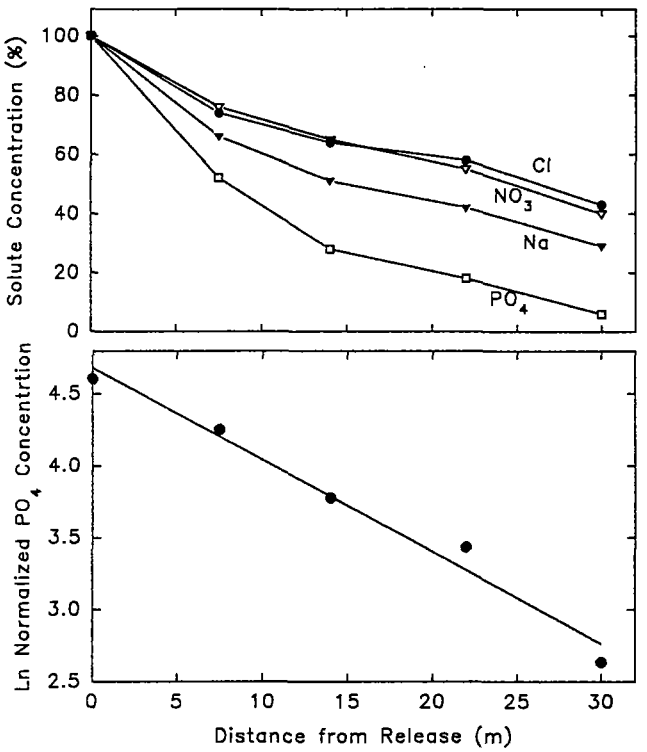

FIGURE 8.5 (Top) Plateau concentrations of solutes versus distance expressed as percentage of upstream concentrations. In this stream NO_3 is relatively abundant and behaves like a conservative solute. PO_4 is taken up from solution. (Bottom) Semi-log plot of PO_4 concentration versus distance. The slope of this line is the PO_4 uptake rate.

where C_{N0} is the theoretical concentration at the release site and x is distance downstream from the release site. Taking the logarithm of both sides of this equation gives

$$\ln(C_N) = \ln(C_{N0}) - k_C x. \tag{8.11}$$

This is the equation for a straight line with intercept of $\ln(C_{N0})$ and a slope of k_C. So if you use your data to run a regression (or draw a graph) of $\ln(C_N)$ versus x, the slope (k_C) will be an estimate of the uptake rate per unit distance. However, be aware that there are lots of simplifying assumptions in doing this, for example, first-order (linear) uptake, no remineralization of added nutrient, and no saturation of uptake processes.

C. Computer Simulation

There are various computer models that can be used to simulate the results of your experiment. A fairly straightforward FORTRAN model can be obtained for free by writing the senior author of this chapter.[2] This model should run on most DOS-type machines and with just about any FORTRAN compiler. This simulation will allow you to calculate dispersion (D), the rate of solute exchange with the transient storage zone (α), and the size of the transient storage zone (A_S).

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?

V. MATERIALS AND SUPPLIES

Laboratory Materials

Beaker (for weighing salt)
Carboy for stock solution of solutes
Conservative solute (noniodized table salt)
Containers for standards
Distilled water
Graduated cylinders (100 ml and 1000 ml)
Nonconservative solute

Lab Equipment

Analytical instruments (for measuring solute concentrations)
Computer (optional)
Electronic balance (±0.01 g)

[2]Dr. J. R. Webster. Please send a blank floppy disk.

Field Materials

Bucket
Calibrated pipet tips
Flagging tape
Graduated cylinder (100 ml)
Mariotte bottle: carboy, rubber stopper, plastic tube, rubber tubing, plastic connectors
Meter stick
Permanent marking pen
Sample bottles
Squirt bottle with distilled water
Stand for Mariotte bottle
Stopwatches
Tape measure (50–100 m)
Thermometer
Velocity meter (optional)
Water-resistant paper or notebook, pencils

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