

Concepts and methods for assessing solute dynamics in stream ecosystems

STREAM SOLUTE WORKSHOP¹

The University of Mississippi, February 1-5, 1989

Abstract. A stream solute workshop was held February 1-5, 1989, at The University of Mississippi with the goals of 1) suggesting a conceptual model for stream solute studies that integrates physical, chemical, and biological processes, and 2) identifying advantages and limitations of various methods for studying solute transport and exchanges. Solute dynamics refers to the spatial and temporal patterns of transport and transfers of materials that are chemically dissolved in water. Solute transport and exchange processes can be described by solute transport equations that relate solute concentration to advection, dispersion, groundwater and tributary inputs, transient storage zones, and biotic and abiotic transformations. Studies can be based on these model equations even if a full simulation of a particular system is not attempted. Although no common methodological approach can serve every investigation of solute dynamics, experimental approaches represent a range from greatest control and least realism to least control and greatest realism. The model parameters describe processes that can be investigated in laboratory, chamber, and flume experiments designed to reduce confounding experimental variables. Whole-stream studies, particularly solute injection experiments, provide estimates of solute transfer to and from the water column and can be used to calibrate the simulation models. Transport and transfer models can link experimental results obtained at different scales and increase the opportunity for inter-site comparisons and the extrapolation of results between laboratory, chamber, flume, and whole-stream studies.

Key words: solute, stream, retention, model, nutrient, solute injection, conservative tracer, scaling.

It has been said that streams are the gutters down which flow the ruins of continents.

L. B. Leopold et al. 1964.

Between each of his excursions through the biota, X lay in the soil and was carried by the rains, inch by inch, downhill. Living plants retarded the wash by impounding atoms; dead plants by locking them to their decayed tissues. Animals ate the plants and carried them briefly uphill or downhill, depending on whether they died or defecated higher or lower than they fed.

A. Leopold 1949

Aldo Leopold continued his story of atom X's journey to the sea by describing X's ride downstream during a spring freshet, "... losing more altitude each hour than heretofore in a century". However, the ride in the stream was not a gutter-slide but was broken by a stop on the river bank. Thus even in the stream, the journey to the sea occurred in a "rolling motion" (Leo-

pold 1941). These contrasting views of streams, as gutters or as ecosystems, have probably motivated many studies of materials carried in stream water.

In addition to being of scientific interest and aesthetic value, streams provide many services including sources of drinking, irrigation, and cooling water; hydropower; commercial transportation; recreation; food; and waste disposal (Meyer et al. 1988). An understanding of processes affecting solutes is essential to maintaining the multiple uses of streams. For example, nutrients may limit stream productivity, thereby affecting food sources and recreational values. Anthropogenic wastes can reduce water quality, depreciating the value of streams for other uses. The ability of streams to assimilate or degrade wastes depends on the maintenance of ecosystem integrity (*sensu* Cairns 1977). Solute transport links terrestrial and aquatic systems and upstream and downstream aquatic systems (Meyer et al. 1988), and may be used as an indicator of effects of disturbance on watersheds (Likens et al. 1970, 1977). In order to attribute disturbance effects to terrestrial processes, we need to understand in-stream processes that occur between the time water enters the stream and reaches the point where samples

¹ Correspondence to: Nicholas G. Aumen, Freshwater Biology Program, Dept. of Biology, The University of Mississippi, University, Mississippi 38677 USA.

are taken (Bencala 1984, Webster and Swank 1985).

The goals of this manuscript, which was derived from a workshop held February 1-5, 1989, at the University of Mississippi, were to: (1) suggest a conceptual model for stream solute studies that integrates physical, chemical, and biological processes; and (2) identify advantages and limitations of various methodological and analytical approaches.

Overview of Stream Solute Studies

Solute dynamics refers to the spatial and temporal patterns of transport and transfer of materials that are chemically dissolved in water. Solute dynamics are coupled to physical movements of water in all ecosystems. In streams, this coupling is expressed in the nutrient spiraling concept (Webster and Patten 1979, Newbold et al. 1983a). As materials cycle among biotic and abiotic components of the stream ecosystem, they are subject to downstream transport. Thus the cycles closely resemble spirals. While upstream movements such as eddies, fish migration, and flight of adult aquatic insects certainly exist, net fluxes in stream ecosystems are usually in the downstream direction.

Differentiation between hydrologic and non-hydrologic processes is critical to an understanding of solute dynamics (Fig. 1). Downstream transport processes physically deliver solutes to reactive sites. These transport processes can be conceptually distinguished from exchanges between various reactive sites. Exchanges between sites may include chemical transformations (i.e., changes in chemical species), changes in physical state such as phase changes, sorption and desorption, and biological processes such as algal or microbial nutrient uptake, microbial oxidation and reduction, and invertebrate consumption of algae. Benthic uptake occurs when materials are transferred from solution in the water column to the streambed, which is stationary relative to stream water. Transfer in the other direction, from streambed to water column, results in release of materials to transport. Retention is the net difference between input and release.

Dissolved substances in streams have been classified in various ways. For example, nutrient solutes necessary for plant reproduction and

growth may be either limiting or non-limiting. Limiting nutrients, by definition, occur in concentrations too low to meet biological demand (Liebig 1855). Other substances dissolved in stream water may be inhibitory to growth or lethal to stream organisms.

Studies of stream solutes have commonly addressed nutrient dynamics owing to their importance in regulating biological processes. Nutrient limitation of primary production in streams has been demonstrated by many studies (Stockner and Shortreed 1976, 1978, Elwood et al. 1981b, Peterson et al. 1983, Triska et al. 1983, Peterson et al. 1985, Tate 1985, Grimm and Fisher 1986, Perrin et al. 1987, Pringle 1987). Primary production in headwater streams may be limited by light and insensitive to nutrient enrichment (Gregory 1980, Lowe et al. 1986). Although decomposition is generally faster in nutrient-rich streams, laboratory and field enrichment studies have given conflicting evidence as to whether nutrients limit decomposition (reviewed by Webster and Benfield 1986). Peterson et al. (1985) suggested that nutrient effects on decomposition may be related to nutrient availability in decomposing material, as is the case in terrestrial systems (Melillo et al. 1982). Decomposition of refractory materials such as oak leaves (Elwood et al. 1981b), wood (Aumen et al. 1983, 1985), or peat (Peterson et al. 1985) may be limited by nutrient supply, whereas labile materials may contain sufficient nutrients to support rapid decomposition regardless of water column nutrient levels.

Stream solutes can also be categorized with regard to their biological or chemical reactivity. Substances used by organisms or otherwise changed either biotically or abiotically are called non-conservative (reactive). Conservative (non-reactive) solutes include essential nutrients that are so abundant as to not be altered substantially by biological demand, or substances that are not usually modified chemically. Conservative and non-conservative solutes undergo dispersion, dilution, and diffusion but conservative solutes are not significantly removed from solution. For example, chloride is an essential nutrient that is widely used as a conservative hydrologic tracer (Bencala 1984). However, it is important to note that at one time or place a particular solute may be conservative, while at another point the same solute may be reactive (Bencala and McKnight 1987).

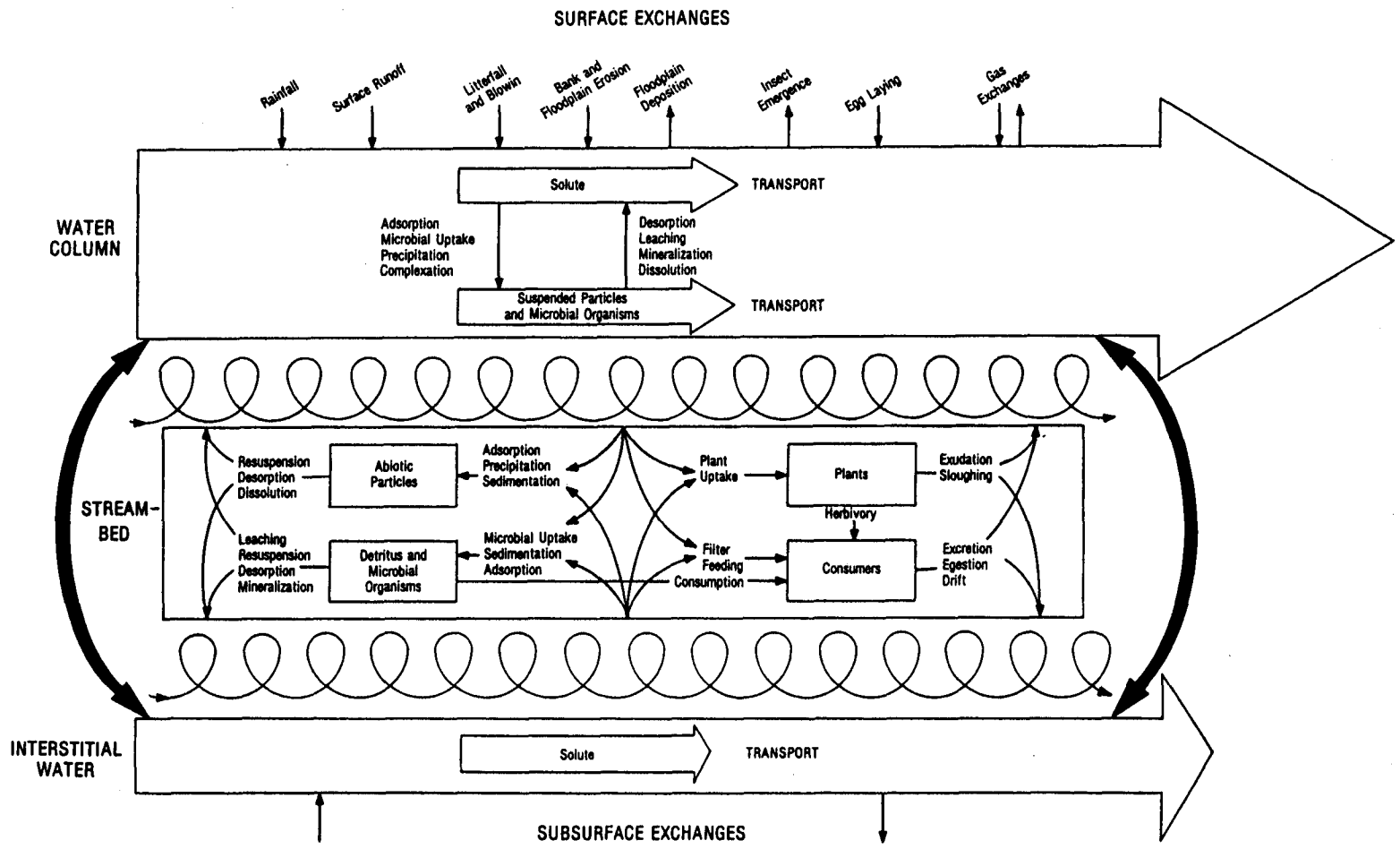


FIG. 1. Conceptual diagram of solute processes in streams, many of which are discussed in this paper. The two spirals represent the continuous exchange of solutes and particle-bound chemicals between the streambed and water column and between the streambed and interstitial water. Materials in the water column and interstitial water are moving downstream, while the streambed materials are stationary.

TABLE 1. Definition of symbols used in text and equations. Units: M = mass, L = length, V = volume (=L³), T = time.

Symbol	Unit	Definition
A	L ²	stream cross sectional area
α	T ⁻¹	storage zone exchange coefficient
A _s	L ²	storage zone cross sectional area
C	M V ⁻¹	solute concentration
C _i	M V ⁻¹	injection solution solute concentration
C ₀	M V ⁻¹	solute concentration at x = 0
C _b	M V ⁻¹	background solute concentration in stream water
C _B	M L ⁻²	solute concentration in benthic compartment
C _{B'}	M M ⁻¹	element concentration in periphyton
C _L	M V ⁻¹	lateral input solute concentration
C _P	M V ⁻¹	plateau solute concentration during steady injection
C _S	M V ⁻¹	storage zone solute concentration
C _{S'}	M L ⁻²	element concentration in sediment
D	L ² T ⁻¹	longitudinal dispersion coefficient
F _w	M T ⁻¹	downstream solute flux
h	L	stream water depth
k _B	T ⁻¹	release rate coefficient from benthic compartment
k _C	T ⁻¹	first-order uptake rate coefficient
K _{dB}	V M ⁻¹	periphyton : water distribution coefficient
K _{ds}	V M ⁻¹	sediment : water distribution coefficient
K _S	M V ⁻¹	half saturation constant for uptake
λ_B	T ⁻¹	first-order coefficient for water/periphyton exchange
λ_S	T ⁻¹	first-order coefficient for water/sediment exchange
Q	V T ⁻¹	stream discharge
Q _i	V T ⁻¹	injection solution discharge
Q _L	V T ⁻¹ L ⁻¹	lateral inflow per unit length of stream
ρ_B	M V ⁻¹	periphyton mass per unit volume of stream water
ρ_M	M V ⁻¹	sediment mass per unit volume of microcosm
ρ_S	M V ⁻¹	sediment mass per unit volume of stream water
S _w	L	uptake length
t	T	time
U	M L ⁻² T ⁻¹	solute uptake rate per unit area of stream bottom
u	L T ⁻¹	water velocity
U _{max}	M L ⁻² T ⁻¹	maximum uptake rate at saturating solute concentration
v _i	L T ⁻¹	mass transfer coefficient from water to benthic compartment
w	L	stream width
x	L	downstream distance

Solute studies of streams may be viewed at a variety of spatial and temporal scales (Frissell et al. 1986, Minshall 1988, Pringle et al. 1988). The geomorphology of drainages is reflected in channel structures created by fluvial process occurring at various recurrence intervals and areal extents. On the basis of geomorphic processes, Gregory et al. (in press) defined six spatial scales for streams, ranging from small particles to entire drainages. Experiments for assessing solute dynamics may be conducted at all of these spatial scales. For example, microcosms may be used to represent patches of substrates, while whole-

stream nutrient injections commonly include one or more channels units (e.g., riffles, pools, rapids, cascades) and may encompass entire reaches. Similarly, durations of solute dynamics experiments commonly are limited to hours or days, whereas there is a greater range of temporal scales in nature.

Modeling Solute Dynamics in Streams

Solute transport and exchange processes can be described by equations that relate solute concentrations to advection, dispersion, ground-

water and tributary inputs, transient storage, and biotic and abiotic transformations. Our discussion of model equations is confined to the one-dimensional case. In adopting this simplification from the generalized three-dimensional problem, the uniformity of cross-sectional and vertical parameters is an inherent assumption that is not always appropriate. Fully developed three-dimensional treatments of physical transport have been presented by Fischer et al. (1979). All model terms used in this paper are defined in Table 1.

Description of model equations

The linkage between solute reactions and transformations and downstream transport in streams has been incorporated in several models (Bencala and Walters 1983, Newbold et al. 1983a, 1983b, Kuwabara et al. 1984). These models are based on equations relating solute concentrations to advection and dispersion in uniform channels with constant discharge:

$$\frac{\partial C}{\partial t} = \underbrace{-u \frac{\partial C}{\partial x}}_{\text{Advection}} + \underbrace{D \frac{\partial^2 C}{\partial x^2}}_{\text{Dispersion}} \quad (1)$$

where C is solute concentration, t is time, x is distance, u is water velocity ($=Q/A$, discharge/cross sectional area), and D is a dispersion coefficient.

To include groundwater and tributary inputs, transient storage zones, and variability in channel morphometry, appropriate terms can be added to the equations and a second equation added for storage-zone solute concentration:

$$\begin{aligned} \frac{\partial C}{\partial t} = & -\frac{Q}{A} \frac{\partial C}{\partial x} + \frac{1}{A} \frac{\partial}{\partial x} \left[AD \frac{\partial C}{\partial x} \right] \\ & + \underbrace{\frac{Q_L}{A} (C_L - C)}_{\text{Lateral flux}} + \underbrace{\alpha (C_s - C)}_{\text{Transient storage}} \\ \frac{\partial C_s}{\partial t} = & -\alpha \frac{A}{A_s} (C_s - C) \end{aligned} \quad (2)$$

where Q_L is the lateral inflow per unit length of stream, C_L is the solute concentration in lateral inputs, C_s is the solute concentration in transient storage zones, A_s is the cross-sectional area of the storage zone, and α is a coefficient

for storage zone exchange. Transient storage refers to the temporary retention of solutes in zones of nearly stationary water and the eventual movement of that water back to the stream channel (Bencala and Walters 1983, Bencala 1984).

This model can be used for conservative solutes (Bencala and Walters 1983). For non-conservative solutes, the model must be modified by adding terms to simulate solute transfers. These terms can have a variety of forms and complexity depending on the type of solute and the use of the model. If it is unnecessary to account for solute concentration in benthic compartments, biotic and abiotic retention may be modeled as a first-order function:

$$\begin{aligned} \frac{\partial C}{\partial t} = & -\frac{Q}{A} \frac{\partial C}{\partial x} + \frac{1}{A} \frac{\partial}{\partial x} \left[AD \frac{\partial C}{\partial x} \right] \\ & - \underbrace{k_c C}_{\text{First order retention}} \end{aligned} \quad (3)$$

where k_c is an overall uptake rate coefficient. Normally, however, solute accumulates in benthic compartments and the release of solute back to the water column must be accounted for. If only a single benthic compartment with first-order release is considered, the model becomes:

$$\begin{aligned} \frac{\partial C}{\partial t} = & -\frac{Q}{A} \frac{\partial C}{\partial x} + \frac{1}{A} \frac{\partial}{\partial x} \left[AD \frac{\partial C}{\partial x} \right] \\ & - k_c C + \underbrace{\frac{1}{h} k_b C_b}_{\text{Benthic flux}} \\ \frac{\partial C_b}{\partial t} = & h k_c C - k_b C_b \end{aligned} \quad (4)$$

where C is water column solute concentration (mass/volume), C_b is benthic concentration (mass/area), h is water column depth, and k_c and k_b are first-order exchange rate coefficients. This general form, expanded to encompass multiple water column and benthic compartments, has been used to simulate ^{32}P dynamics in a stream (Newbold et al. 1983a).

The uptake rate coefficient, k_c , describes uptake on a volumetric basis instead of as a flux to the stream bottom. Exchanges across interfaces (such as a sediment/water) are often de-

scribed in terms of a mass transfer coefficient, v_t (O'Conner 1988), which has units of length/time and may be thought of as the vertical velocity at which solute migrates through the sediment/water interface. The mass transfer coefficient is related to the uptake rate coefficient, k_c , through depth (h), so that $v_t = hk_c$. Thus Equation 4 can be written:

$$\begin{aligned} \frac{\partial C}{\partial t} &= -\frac{Q}{A} \frac{\partial C}{\partial x} + \frac{1}{A} \frac{\partial}{\partial x} \left[AD \frac{\partial C}{\partial x} \right] \\ &\quad - \frac{v_t}{h} C + \frac{1}{h} k_B C_B \\ \frac{\partial C_B}{\partial t} &= v_t C - k_c C_B \end{aligned} \quad (5)$$

The advantage of v_t over k is that it more nearly describes abiotic uptake and under certain circumstances may even be estimated from the hydraulic characteristics of the stream (O'Conner 1988). Thus, v_t may be expected to remain relatively constant under changes in water column depth, allowing a single value to suffice in a model that might require varying values of k . Moreover, it is a parameter that may be comparable between streams of different depth.

In some cases it may be preferable to describe uptake in relation to the mass of exposed sediment, organic matter, or biomass in stream sediments. Kuwabara et al. (1984) described stream transport of copper by incorporating first order mass transfer equations for periphyton and sediment reactions:

$$\begin{aligned} \frac{\partial C}{\partial t} &= -\frac{Q}{A} \frac{\partial C}{\partial x} + \frac{1}{A} \frac{\partial}{\partial x} \left[AD \frac{\partial C}{\partial x} \right] \\ &\quad - \underbrace{\rho_B \frac{\partial C_B}{\partial t}}_{\text{Periphyton retention}} - \underbrace{\rho_S \frac{\partial C_S}{\partial t}}_{\text{Sediment retention}} \\ \frac{\partial C_B}{\partial t} &= -\lambda_B (C_B - K_{dB} C) \\ \frac{\partial C_S}{\partial t} &= -\lambda_S (C_S - K_{dS} C) \end{aligned} \quad (6)$$

where C_B is solute concentration in periphyton and C_S is solute concentration in sediments. The coefficients ρ_B and ρ_S reflect the mass of periphyton and sediment per unit overlying water,

and λ_B and λ_S are first-order exchange rate coefficients. The K_{dB} and K_{dS} coefficients are partition coefficients, expressing the equilibrium ratios of solute concentration between periphyton and water column, and between sediment and the water column. Limitations to the applicability of this simplified first-order representation are clearly present when competitive solute uptake, changes in community structure, and mechanisms of tolerance and adaptation are significant (Kuwabara et al., in press).

If uptake is not linear with concentration, it may be necessary to use different uptake functions, such as the Monod (or Michaelis-Menten) formulation, which is frequently used for algal uptake (Bowie et al. 1985). For example, the uptake term, $k_c C$, in Equation 4 could be replaced by U/h where:

$$U = \frac{U_{\max} C}{K_s + C} \quad (7)$$

and U_{\max} is the maximum uptake per unit area of stream bottom and K_s is the half-saturation constant, i.e., the solute concentration at which uptake is one-half the maximum. The parameters U_{\max} and K_s may vary according to the specific populations of benthic organisms responsible for uptake.

Use of the Monod formulation is for empirical convenience and may not directly represent algal uptake kinetics. The variety of organisms and processes responsible for uptake, potential diffusion limitation of nutrients to and into microbial mats or biofilms, and potential effects of changing internal cell concentrations all limit the direct applicability of Monod uptake kinetics. Several other non-linear functions may also be used (Kuwabara and Helliker 1988). For example, if solute uptake is primarily by physical sorption, then non-linear sorption kinetics may be appropriate (Bencala 1984). Non-linear kinetics are not necessary when tracers are used at levels low enough to have an insignificant impact on concentration of the modeled solute (Newbold et al. 1983a). In this case, the model does not describe responses of nutrient uptake to changes in concentration but rather a simple mixing process of the tracer in which actual concentrations of the modeled solute are assumed to remain constant over the duration of the experiment. Thus the tracer is extremely effective in estimating exchange rates under a

given set of conditions but gives no information about responses to changing nutrient concentrations.

These models provide a basis to understand field studies and laboratory experiments. Many model parameters can be estimated by process-level experiments such as those described below. Then, using data from a short-term solute injection, the model can be calibrated. This involves adjusting unmeasured parameters to produce a simulation that best fits the field data. While modeling cannot substitute for understanding, the exercises can contribute in two ways to our understanding. First, the actual numerical values of process parameters can be used to quantitatively compare streams. Second, models that are sufficiently rooted in fundamental processes can be used to connect our understanding of processes at differing scales. Ultimately, solute dynamics in streams are characterized by (1) the tight coupling of transport and transfer processes and (2) the diversity of physical, chemical, and biological processes affecting solutes. The former is captured in simple models, but the latter requires complex, flexible model structure.

Model Parameters and Nutrient Cycling

From the parameters in Equations 4, 5, and 6, it is possible to derive various measures of nutrient uptake and other information about nutrient cycling in streams. One reasonable expression of biotic or abiotic uptake is the total flux of nutrient from the water column to the stream bottom (U), expressed on the basis of stream bottom area (e.g., $\text{mg m}^{-2} \text{h}^{-1}$). This quantity refers to uptake under normal nutrient concentrations. Under these conditions, nutrients may be cycled back to the water column at a nearly equal rate (Newbold et al. 1983a); thus U refers only to gross uptake rather than retention.

Under many circumstances it would be possible to obtain an estimate of U from a solute injection study as described below. Once experimental data have been used to quantify model parameters (see below), U can be calculated. Using Equation 5, for example, uptake would be $U = v_i C_b$, where C_b is the background (prior to experiment) nutrient concentration. Alternatively, U could be calculated from Equation 6 as:

$$U = (\lambda_b \rho_b K_{dB} + \lambda_s \rho_s K_{dS}) C_b \quad (8)$$

Estimation of U from a solute injection has several limitations. First, if uptake is saturated at C_b , then injected solute will behave as a conservative tracer and no uptake parameters can be estimated. Second, no distinction is made here between biotic and abiotic uptake. For a nutrient with a high affinity for surface complexation or adsorption, such as phosphate or ammonium, the uptake of a nutrient injected at substantially elevated concentrations may be largely controlled by abiotic processes even if biotic uptake is important at the normal concentration. Finally, the amount of exchangeable nutrient in the stream bottom must be accounted for in fitting the model parameters. This quantity may be measured independently or estimated by the model fitting process.

For comparisons of uptake of different nutrients, the mass transfer coefficient, v_i , may be a more useful parameter than gross uptake. This might also be the case when modeling is based on a tracer release and the coefficients are determined without reference to actual nutrient concentrations. The transfer coefficient is related to uptake by $v_i = U/C_b$. That is, it represents uptake normalized by the concentration in the water column. If uptake from the stream is first order, the transfer coefficient can be taken directly from the model as in Equation 5. For nonlinear uptake, the transfer coefficient can be evaluated from U and C_b by substituting C_b into the uptake function (e.g., Equation 7).

Newbold et al. (1981, 1983a) and Elwood et al. (1983) described spiralling length as the average distance an atom travels during one complete cycle from the dissolved state in the water column, to a streambed compartment, and eventually back to the water column. This measure was proposed to describe nutrient utilization efficiency of a stream, i.e., the spiralling length becomes shorter as nutrients are more intensely used. Spiralling length consists of two parts: uptake length is the distance traveled in dissolved form, and turnover length is the sum of distances traveled in particulate form. We will focus here on uptake length, which has been found to be much longer than turnover length for phosphorus in systems studied by Newbold et al. (1983a) and Mulholland et al. (1985b).

Uptake length, S_w , is related to nutrient up-

take, U , by $S_w = (F_w w)/U$, in which F_w (mass/time) is the downstream flux of dissolved nutrient available for uptake, and w is the stream width. However, uptake length can also be calculated directly from model parameters. For example, using Equation 4, $S_w = Q/(k_c A)$. Since Q/A is water velocity, u , $S_w = u/k_c$ (Newbold et al. 1983a). The inverse of k_c is the average turnover time of a molecule in the water column and is equivalent to turnover times used in limnological literature (Wright and Hobbie 1966, Lean and Nalewajko 1979).

The indices k_c and S_w can also be derived from the parameters of more complex models using the same principle applied above for computing nutrient uptake, U . This involves computation of an effective value for k_c , such that $hk_c C = U$. For example, if the Monod uptake is used, $k_c = U_{max}/[h(K_s + C)]$. Note that the uptake length is independent of nutrient concentration when the relation between uptake and nutrient concentration is linear ($C \ll K_s$), but increases linearly with nutrient concentration as uptake becomes saturated ($C \gg K_s$).

The four basic uptake parameters described above, uptake per unit area (U), transfer coefficient (v_t), uptake rate coefficient (k_c), and uptake length (S_w) are all interrelated. If water velocity, depth, and concentration are known, any three can be calculated from the fourth:

$$\begin{aligned} k_c &= \frac{v_t}{h} \\ S_w &= \frac{u}{k_c} = \frac{uh}{v_t} \\ U &= v_t C \end{aligned} \quad (9)$$

The longitudinal rate at which a solute is taken up is related to the uptake length, and under certain conditions, uptake length can be calculated directly from short-term solute injection data without simulation modeling. The conditions are:

1. Channel and flow characteristics are reasonably uniform.
2. Uptake of nutrient by streambed constituents is directly proportional to concentration in the water.
3. Release of nutrient from the bottom does not significantly affect nutrient concentration during the measurement period.

If the above conditions are satisfied, a steady

injection of solute will yield a plateau concentration coincident in time with the plateau of a simultaneous conservative tracer. Failure to achieve a plateau indicates violation of one or more of these conditions. At steady state, the effects of longitudinal dispersion (D) can usually be neglected, and the concentration $C(x)$ of the plateau is given by the following approximate solution of Equation 4:

$$C(x) - C_b = [C_0 - C_b]e^{-k_c(x/u)} \quad (10)$$

in which C_0 is the concentration at $x = 0$, the point of injection, C_b is the background concentration of solute, and velocity, u , has been substituted for Q/A . If the above conditions are met, plateau measurements of $C(x)$ at successive points, x , along the stream can be corrected for dilution using the conservative tracer and fitted as a straight line on a logarithmic scale. The slope of this line is $-k_c/u$, which, from Equation 9, is $1/S_w$ or the inverse of the uptake length.

Direct field estimation of uptake length can be particularly successful with tracer-level releases because the actual quantity released is too small to cause non-linear changes in uptake so that condition (2) is satisfied. A variation of using plateau concentrations involves time-integrating concentration over the entire passage of the release pulse and replacing $C(x)$ with the ratio of the integrated nutrient concentration to the integrated conservative tracer concentration (Newbold et al. 1981). Integration could be used for a relatively short release in which a plateau is not achieved, but this technique is not recommended without independent assurance that conditions (1) and (3) above are satisfied.

Whole-stream Studies of Solute Dynamics

Whole-stream solute injection experiments provide excellent opportunities for understanding the integrated physical, chemical, and biological properties of a stream ecosystem. In a solute injection experiment, a conservative and reactive solute are added to the stream at a known rate and their concentration in the water column is monitored. The advantage of this approach is that both the natural ecological environment and the hydrologic and transport features of the stream are incorporated. Realistic estimates of water and solute transport, retention, and transformation are provided by

solute injection experiments but underlying mechanisms may be more difficult to elucidate.

Advantages and disadvantages of the approach

Experiments in which a conservative tracer is added to a stream can be used to quantify hydrologic parameters such as channel velocity, dispersion coefficient, and subsurface water flux. Because the hyporheic zone can be large (Stanford and Ward 1988) and spatially complex (Triska et al. 1989a), actual mean residence time of water in a stream may be quite different from that obtained from volume and flow measurements in open channels. Valuable information about transient storage and groundwater inputs can be obtained by analyzing spatial and temporal changes in concentrations of an inert tracer added continuously at a well-mixed upstream station. Procedures for these injections are discussed later in this paper.

When a reactive solute is added with a conservative tracer, a variety of topics can be addressed using whole-stream experiments:

- 1) stream responses to solute inputs of relatively short duration and high magnitude, e.g., release of dissolved organic carbon (DOC) during autumn leaf fall (Lush and Hynes 1978, McDowell 1985) or a short-term release due to an industrial accident or failure of a sewage treatment plant;

- 2) stream responses to long-term changes in solute input due to increased rates of atmospheric deposition (Hall et al. 1980), fertilization to increase fish production (Stockner and Shortreed 1978), or eutrophication due to human activity (Peterson et al. 1985);

- 3) uptake and retention rates of solutes that may limit primary production or decomposition rates (Newbold et al. 1983a, 1983b);

- 4) within- or between-site comparisons of solute retention and transformation under realistic conditions (McDowell 1985, Mulholland et al. 1985b, Munn 1989), and comparisons of the dynamics of a variety of solutes such as organic compounds (McDowell 1985) or nutrients (McCull 1974).

Disadvantages of the whole-stream injection technique include: difficulty in replicating experiments; difficulty in demonstrating mechanisms of solute retention or transformation; and difficulty in locating microsites where retention occurs, especially if one is unable to use radioactive tracers. Differences in stream substrate

composition, patterns of groundwater inflows, trends in light intensity and background water chemistry, quantity and composition of periphyton, and other variables are uncontrollable or often not quantifiable. Even when apparent differences in such variables are minimal among a set of reaches or streams, physical and fiscal constraints will often limit the ability to perform replicated experiments.

Whole-stream solute injections provide excellent data on rates of retention or transformation, and when paired with laboratory experiments as described in the following section, can provide insight into underlying mechanisms (Meyer 1979, Kuwabara et al. 1984, McDowell 1985). In some cases, results from solute injection experiments can provide evidence for specific mechanisms, e.g., production of nitrate upon injection of ammonium, indicating the presence of nitrification (Richey et al. 1984, Newbold et al. 1983b).

Application of simulation analysis to solute injections

Solute injection experiments can be combined with transport model simulations to estimate hydrologic and solute retention parameters for the stream. This is a more detailed data analysis than simple calculations of uptake length from plateau concentrations described earlier. Quantitative comparisons can be made between streams and among processes at different scales because the models normalize solute retention for parameters such as discharge.

In order to interpret the results of a reactive solute injection, parameters that describe purely physical processes in the channel must first be described. This is accomplished by injecting a conservative solute and using simulations to identify the physical process parameters (Newbold et al. 1981, Chapman 1982, Newbold et al. 1983a, 1983b, Bencala 1984, Jackman et al. 1984/1985). Once determined, hydrologic parameters can be used unchanged in an expanded model that describes the behavior of a simultaneously injected reactive solute. Additional parameters of the expanded model can then be estimated from the reactive solute data. Kuwabara et al. (1984) gave a clear example of how to use experiments and simulations to separate and determine the relative importance of interdependent physical, chemical, and biological processes.

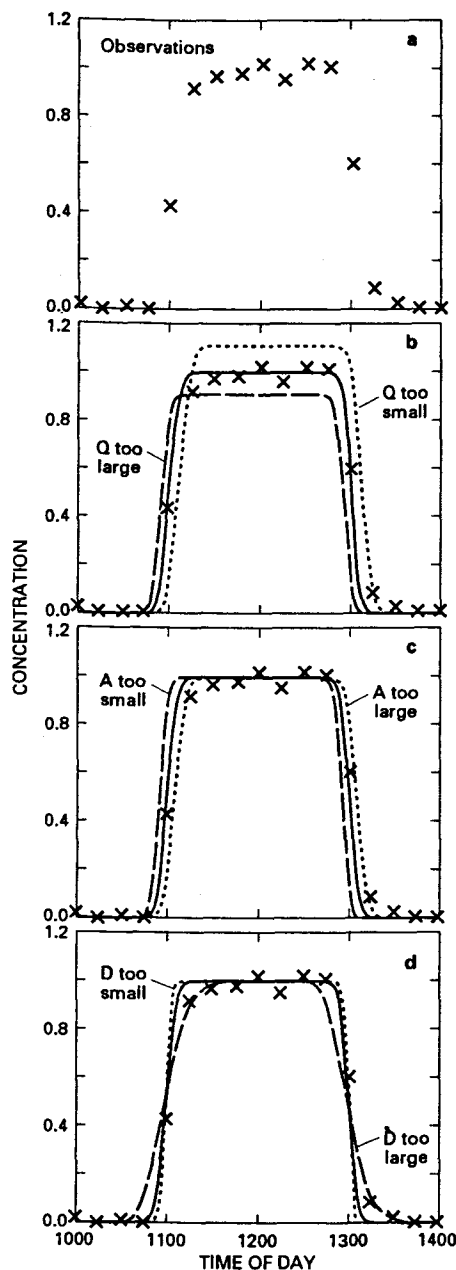


FIG. 2. Hypothetical data from a steady injection of a conservative tracer into a stream channel. The symbols indicate measured concentrations over time at a fixed sampling location downstream from the injection location. Solid, dashed, and dotted lines indicate hypothetical results of simulations using various estimates of Q , A , and D .

The basic equation of transport assuming a one-dimensional system was given in Equation 1. To fully evaluate solute transport, two additional parameters must be known: the initial solute concentration within the study reach and either solute concentration or mass flow at both ends of the study reach. The symbols u and D in Equation 1 specify physical parameters. The approach discussed here is to use concentration data obtained from the experiment and to use simulation of Equation 1 to determine the value of these parameters. This exercise is formally referred to as "parameter identification" or solution of the "inverse problem".

The standard approach is to physically measure parameters and then run a simulation of the process to predict concentrations. These predicted concentrations may then be compared to experimental data to assess the validity of the simulation equations. Parameter identification is the inverse of this procedure. An experiment is completed to determine concentration values and then simulations are run to identify a set of parameter values yielding predicted concentrations similar to the data. The fundamental assumption is that Equation 1 is an appropriate model of the solute transport. The inverse approach can be used to identify the parameters of any physical, chemical, or biological process that can be formulated with appropriate equations, although here we will discuss only how to use simulations of Equation 1 to identify Q , A , and D .

A hypothetical response graph shows the steady injection of a conservative tracer (Fig. 2a) resulting in a steady concentration plateau. The symbols indicate measured concentrations over time at a fixed sampling location. For this situation, identifying the discharge (Q) is straightforward. Equation 11 is the mass-balance for the injected conservative tracer:

$$C_b Q + C_i Q_i = C_p Q \quad (11)$$

where C is concentration and the subscripts are: b , background; p , plateau; i , injection solution. It is assumed that the injection flow does not increase the stream discharge ($Q_i \ll Q$). Equation 12 is the mass-balance solved for Q :

$$Q = \frac{C_i}{C_p - C_b} Q_i \quad (12)$$

With this estimate of Q , numerical solutions of Equation 1 can now be done. In Figure 2b, hy-

pothetical simulations with fixed but arbitrary values of A and D are sketched for three values of A : one too large, one too small, and the estimated value.

The parameters A and D are now identified by trial-and-error comparisons of the simulations to the experimental field data. In Figure 2c, simulations are presented for three values of A with the estimated Q and an arbitrary but fixed D . An estimate for A that is too large results in a low velocity and the simulated pulse arrives too late. Conversely an estimate for A that is too small would simulate the water and solute as moving too rapidly. One therefore iterates between values for A which are alternately too large and too small until a simulation is obtained with an arrival time similar to that of the experimental field data. After A has been estimated, the trial-and-error comparisons can be done with D (Fig. 2d). At this point A may need to be re-estimated using the latest estimate of D .

The method described here for estimating parameter values is subjective, i.e., there are no quantitative measures of goodness of fit or uncertainty in the experimental data. Objective techniques do exist. A good example was presented by Wagner and Gorelick (1986) in which new estimates were made of the parameters found by Bencala and Walters (1983).

Including lateral inflows and transient storage (Equation 2) requires estimating more model parameters. Lateral inflow, Q_L , and lateral inflow solute concentration, C_L , can be estimated algebraically because for both steady-state background and steady-state plateau, masses of both water and solute must balance. The transient storage parameters, A_s and α , are abstractions based on observations of considerable spreading of solute pulses in real stream systems. There are neither actual zones of cross-section A_s nor flow processes exchanging water with rate constant α . The transient storage parameters can be identified by trial and comparison of simulations to observations. Figure 3a shows a hypothetical comparison between simulations with and without the transient storage enhancement. The essential features of the observations are the shoulder of the rising edge and the persistence of the tail concentrations. There is no recognized best procedure for identifying the transient storage parameters; experience suggests that it is effective to test the

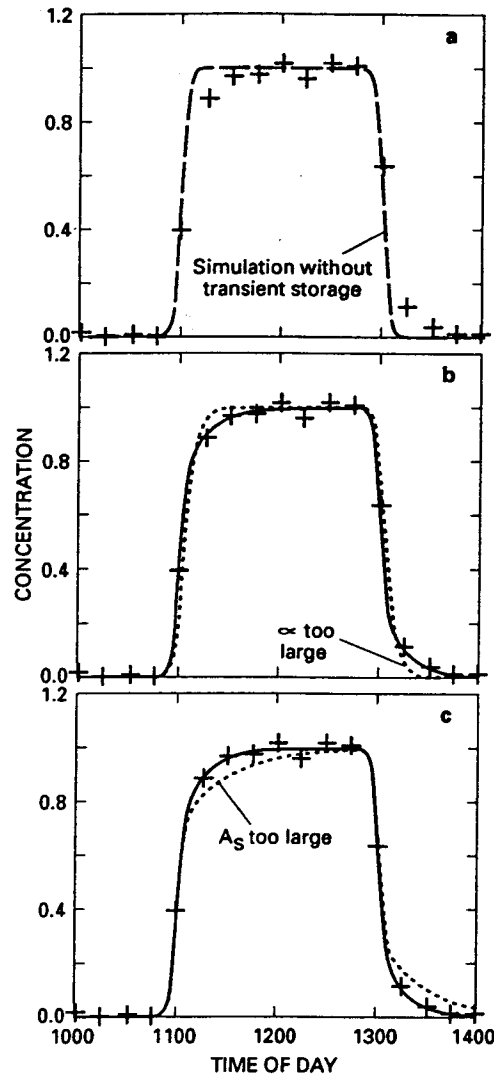


FIG. 3. Hypothetical data from a steady injection of a conservative tracer into a stream channel. The symbols indicate measured concentrations over time at a fixed sampling location downstream from the injection location. Solid, dashed, and dotted lines indicated hypothetical results of simulations using various estimates of transient storage.

exchange coefficient (α) against how fast the shoulder falls away from the vertical (Fig. 3b) and the storage cross-section (A_s) against how slowly the tail returns to the horizontal (Fig. 3c).

In a technical sense, the injection-simulation approach is appealing and powerful because it allows one the opportunity to study the system

in a state of disequilibrium (i.e., studying the system as it responds to a defined solute perturbation). From a more pragmatic point of view, the approach is particularly useful in the upland stream environment because of the nature of physical parameters we wish to identify. Some of the parameters (Q and C_L) are difficult to measure, some parameters (Q_L and A) vary over short distances, and some parameters (α and A_s) are simplifying abstractions.

Simulations based on the partial differential equations of transport are not the only approach to extending hydrologic information from experiments. As one way to more fully appreciate what may or may not be gained with simulations, it may be instructive to compare how the same conservative tracer data were used by different workers. For example, the chloride data used by Bencala (1984) were also used by Triska et al. (1989a, 1989b), and the chloride data used by Jackman et al. (1984/1985) were also used by Kennedy et al. (1984/1985).

Experimental protocol

Use of radioactive and stable isotope tracers.—Studies of the dynamics of reactive solutes in streams may be best approached by additions of either radioactive or stable isotopic tracers. Advantages of using isotopic tracers are that the tracer itself as well as its movement through and dynamics within the system can be measured. Because the detection limits for radioactivity are typically much lower than those for stable isotopes, it is possible to detect radiotracers at much lower levels. Such low level enrichment precludes the possibility that tracer addition alone would affect the uptake. For elements such as nitrogen, however, where radiotracers may be impractical, stable isotopes may be best.

The major limitation of radiotracers is that their use for experimental purposes is limited and may not be approved for release in many streams. It should be possible, however, to use radiotracers in controlled channel and microcosm studies to evaluate kinetics of solute uptake from water at different levels of solute enrichment. Also, stable isotopes such as ^{15}N and ^{34}S which do not require approval can be obtained in highly enriched form. Use of these isotopes in whole stream studies is possible at a tracer level and is economically feasible.

Solute injection techniques.—A second approach is to increase concentrations of solutes of interest above ambient levels. Resulting total concentration relative to concentration present prior to injection is then determined. The advantage of this approach is that special approvals or precautions may not be required for injection of most solutes. The disadvantage is that only net uptake of solutes from water can be measured. Pathways of solute uptake and transfers within streams cannot be followed because the solute cannot be traced once it is lost from stream water. If solute injections are intended to investigate solute dynamics at ambient concentrations, the relation between solute uptake and concentration should be known prior to release. Such information will ensure that injection does not exceed biotic uptake capacity. It is useful to know whether concentrations used are on the linear or saturation portion of the uptake kinetics curve. If linear, natural or background uptake rates can be readily calculated from background concentration and v_i (Equation 9).

Solute injection techniques assume that one tracer used is conservative. Background concentrations of the conservative tracer should be undetectable or low, the tracer should not react chemically or biologically, and it should not compete with other ions for exchange sites. The conservative tracer is injected into the stream along with the reactive solute, most commonly to calculate dilution and dispersion.

Various types of conservative tracers are currently used including chemical salts, fluorescent dyes, and radioactive materials. The most common chemical salts used are chloride, sodium, lithium, potassium, and magnesium. Chloride is generally accepted as the most conservative of commonly available solutes. Chloride can be measured colorimetrically or by ion chromatography, or may be followed in situ using a sensitive conductivity meter, a specific ion electrode, or a transportable autoanalyzer. Various factors can alter the conservative behavior of an ion. For example, chloride is not significantly sorbed by soils at $\text{pH} > 7$, but may be sorbed as stream water becomes more acidic (Kennedy et al. 1984/1985).

Organic dyes such as rhodamine WT are used extensively as conservative tracers. A major advantage of dyes is that very low concentrations can be monitored in the field using fluorom-

eters, and mixing may be observed visually using greater concentrations of dye. Rhodamine WT is conservative in many, but not all, lotic environments. It can be sorbed by streambed sediments (Bencala et al. 1983, Munn and Meyer 1988) and loses fluorescence in streams with low pH. Other commonly used dyes such as fluorescein may photo-degrade and should be avoided.

Multiple tracer additions may be useful in some situations. Fluorescent dye gives a quick estimate of travel time in the field, and simultaneous addition of chloride will provide more accurate estimates of hydrologic parameters. Low concentrations of dyes may interfere with colorimetric analyses of other ions (N. G. Aumen, Univ. of Mississippi, unpublished data), but dyes can be removed by passing samples through reverse-phase cartridges (Laane et al. 1984).

Isotopic hydrologic tracers include deuterium (2H), a stable isotope of hydrogen, or tritium (3H), a radioactive isotope of hydrogen. These isotopes are near-perfect hydrologic tracers because they behave almost identically to water and exhibit truly conservative behavior. They do exhibit isotope effects, although such effects can usually be ignored when measuring dilution, dispersion, and advection of solutes.

Solute injection techniques also involve the addition of reactive solutes that may bind chemically or biologically to the streambed or other surfaces. If the objective of a reactive solute release is to describe solute dynamics (e.g., nutrient cycling) under natural conditions, then it is desirable to keep maximum injected concentrations within or near the natural range. Non-linearities in uptake at high concentrations and potential saturation of uptake capacity can be accounted for, in principle, by appropriate model formulations. However, injections at high concentrations may limit the description of low-level dynamics to the rising and falling limbs of the injection curve. Data from the rising and falling limbs are also useful in describing the effect of interstitial flow and the influence of bed relief (Bencala et al. 1984).

Because elemental ratios can influence uptake dynamics, solute additions should not markedly alter ratios of macro- and micro-nutrients. For example, the ratio of nitrogen to phosphorus in stream water can alter retention potentials of these elements (Grimm and Fisher

1986). This problem is most critical when N:P ratio is between 10 and 20 (Shanz and Juon 1983). Another example is when there is competitive uptake between the injected solute and another solute (e.g., arsenate and phosphate; Kuwabara et al., in press). One solution is to inject multiple solutes to maintain appropriate element ratios. Because the solubility and sorption of many compounds change with pH, the solute injected should be in a form that does not alter the pH. Subsequent reactions may also alter pH, such as added ammonium undergoing nitrification or added limiting nutrient altering photosynthesis.

Spike or short-term pulse releases of solutes are useful for studies to measure general channel flow or the potential for solute removal from stream water. Continuous releases of solute can provide quantitative data on loss rates from stream water and flow rates through stream channels. Data from this type of release can be analyzed using the models described elsewhere in this manuscript. Continuous releases are easiest to analyze when conducted during stable flow periods. Long-term releases (days to months) may be used to gain information about storage and sorption processes on long time scales (Bencala et al. 1984), or to enrich the stream and measure the resulting trophic response (Peterson et al. 1985).

The appropriate reach length may also vary, although one should use the minimum channel length needed for complete mixing of the solutes and for analytically detectable removal to occur. Because hyporheic influences are minimized in short reaches, transient storage is a lesser problem than in long reaches. Solute injections may be inappropriate for assessing effects of small-scale spatial heterogeneity on solute dynamics because variability is usually on the scale of meters or less (see section on spatial scales).

The duration of a solute injection should be sufficient for mixing and even distribution within the stream reach but short enough to avoid saturation of chemical and biological retention sites. Seasonal (Mulholland et al. 1985b) and diel (Kaplan and Bott 1982) variation in solute retention should be considered in experimental design, data analysis, and data interpretation, particularly when comparing streams.

Both physiological and successional state of

the biota may influence solute injection experiments. Although the technique assumes that biota have constant solute uptake potential, algae vary diurnally in solute uptake, and biotic retention sites may saturate early during the solute release. If solute is added over a number of days, both day and night samples are essential. Successional state of biota can also alter the potential for solute uptake (Grimm 1987); hence time since the last storm, last solute release, or other disturbance should be considered.

Other whole-stream methods.—A mass balance approach to solute injection studies can be a valuable tool for estimating ecosystem response. The load of amended solute is the average, background-corrected, solute concentration within a specified interval, multiplied by that time interval and by discharge. Net retention for the total reach is the difference between the load at the injection point and that at the base of the reach. The mass balance approach is open-ended temporally, and can be either cumulative or interval specific. For short-term applications such as estimating mass in transient storage or instantaneous biotic response to nutrient loading, the minimum injection time is that required for the conservative tracer to attain plateau concentration. For long-term applications such as solute retention associated with biomass enhancement following amendment of a limiting nutrient, the investigator must subjectively determine the duration of each injection.

Experimental studies involving long-term nutrient enrichment of streams may be useful in some systems to predict results of future human-related enrichment on ecosystems, to ascertain how elemental cycles adjust to inputs of specific nutrients, and to determine how trophic structure is modified by long-term enrichment. The mechanics of the enrichment will vary according to characteristics of the stream, such as background nutrient levels, discharge, geomorphology, and riparian structure. It may be desirable to maintain the nutrient addition at levels that the stream encounters normally (e.g., during runoff), rather than exposing the stream to unrealistically high nutrient loading. Some enrichments may emphasize augmentation of specific nutrients (Peterson et al. 1985), whereas others may attempt to maintain typical nutrient ratios (Perrin et al. 1987). Adjustment

of release rate to changes in discharge is important to maintain the enrichment effect, unless simulation of constant inflow sources is being attempted.

Identification of Processes Underlying Solute Dynamics

Although whole-stream studies are needed to understand solute dynamics in an ecosystem context, isolating processes of interest from other confounding ones may be difficult in whole streams. Subsystem-level studies are usually necessary to resolve individual solute transfers and transformations by controlling confounding processes. The most common experimental approaches to isolation of individual processes are laboratory, in situ enclosure (chamber), and artificial channel (flume) methods.

Physical, chemical, and biological transformations can regulate non-conservative solute retention in streams. Nutrients such as nitrogen, phosphorus, sulfur, some classes of dissolved organic material, and certain trace metals are especially susceptible to biologically-mediated transformation. Both assimilatory and dissimilatory biological processes can affect solute dynamics. Assimilatory processes occur when an organism takes up a solute for use in growth and metabolism. Dissimilatory processes involve use of nutrients either as energy sources (oxidation reactions) or as alternative electron acceptors (reduction reactions) when oxygen is absent. These processes are often associated with the sediment-water interface or the hyporheic zone in streams, and the specific reactions are closely linked to the redox potential of the environment. Chemical processes of potential importance include adsorption and desorption, complexation and dissociation, precipitation and dissolution, photolysis, and oxidation and reduction (see Kuwabara and Heliker 1988).

Questions addressed by process-level studies

Laboratory methods.—The relative importance of biotic versus abiotic mechanisms of solute retention can be determined by modifying or eliminating biological activity using heat, radiation, or chemical sterilization (Gregory 1978, Meyer 1979, Dahm 1981, Elwood et al. 1981a,

McDowell 1985), or the addition of metabolic inhibitors (Duff et al. 1984, Mulholland et al. 1984, Perkins et al. 1986). Such treatments are difficult *in vivo* because of the large scale of field studies or because of problems associated with the use of metabolic poisons in natural settings. Laboratory systems also have been used to determine the equilibrium phosphorus concentration (EPC), the concentration at which phosphorus is neither adsorbed nor desorbed from sediments (Taylor and Kunishi 1971, Meyer 1979, Klotz 1985).

Isolation of individual microbial populations in the laboratory can help resolve microbial and algal uptake mechanisms. Uptake kinetics studies are especially useful in understanding population-level processes and have been widely used in microbiology and phycology to describe uptake and transport of solutes across membranes (Eppley and Coatsworth 1968, MacIsaac and Dugdale 1969, Brown et al. 1978, Halterman and Toetz 1984, Paris and Rogers 1986). Kinetic parameters determined in the laboratory may include reaction order, half-saturation constant (K_s) and maximum uptake rate (V_{max}) of populations or simple assemblages. These kinetic parameters may be affected by chemical interactions (e.g., solute speciation and competitive ion uptake), the composition and metabolic state of the sample populations, and hydrodynamics under conditions of diffusion limited uptake.

Models of reaction kinetics designed for specific enzymatic reactions or individual populations (e.g., the Michaelis-Menten model) should be applied with caution to complex biological assemblages. However, kinetic studies have increased understanding of community nutrient uptake and nutrient-growth relations in lakes and marine systems (Rhee 1980, Suttle and Harrison 1988) and stream-side flumes (Bothwell 1985, Kim et al., *in press*). Algal assemblages may occur in patchy distributions in streams (Fisher et al. 1982, Pringle et al. 1988); thus large experimental units may be appropriate for uptake kinetics studies at the community level.

Structural integrity of epibenthic microbial layers is important to metabolism of lotic microorganisms (Ford and Lock 1985, 1987) and may affect solute uptake and release processes in streams. Therefore, solute dynamics of complex assemblages may not be adequately de-

scribed by batch or continuous culture methods. Uptake kinetics may need to be measured in field chambers (see below) rather than in the laboratory.

In situ chamber methods.—While laboratory methods permit control of experimental variables, realism may be sacrificed to an unacceptable extent for some applications. *In situ* chambers incorporate some in-stream realism (e.g., temperature, light, and possibly current velocity) but also maintain a level of control by isolating discrete units of stream channel for further manipulation. This approach enables examination of solute dynamics of natural assemblages or patches (Dahm 1981, Grimm and Fisher 1984, Pringle 1985, Aumen et al. 1990), determination of solute effects on metabolic activity (Grimm and Fisher 1986), application of kinetic models to intact assemblages, and isolation of solute transfers across the sediment-water interface (Teal and Kanwisher 1961, Everest and Davies 1979). A disadvantage of enclosures (relative to flumes) is that the isolated material is cut off from renewal and removal effects of water movement (Whitford and Schumaker 1961, 1964). Although current velocity can be reproduced with submersible pumps or stirring devices, chemical conditions may change dramatically during incubation. This problem can be reduced by limiting incubation time.

Streams are a composite of different habitats or patches (Pringle et al. 1988, Townsend 1989). With chambers, it is possible to evaluate the relative importance of patches by placing habitat components (e.g., leaves, wood, periphyton, rocks, macrophytes, fine sediments) in individual chambers with stream water. One can then compare effects of each component on changes in stream water nutrient concentration (Dahm 1981, Duff et al. 1984, Aumen et al. 1990). Because of isolation from the main stream, it is more feasible to use radiolabeled materials than in whole-stream studies. Assumptions of all procedures are that transfer of isolated patches into chambers does not alter uptake rates and that sums of patch uptake equal uptake by entire stream channels. One disadvantage is that by isolating patches, exchanges at patch interfaces are not measured (Naiman et al. 1988).

Chamber methods are also appropriate for measuring short-term metabolic responses of

stream organisms to nutrient additions. Measurements of photosynthesis and respiration in streams have long relied on chambers with recirculating water (Bott et al. 1978). Nutrient additions to chambers and measurement of metabolic responses can help identify nutrients that stimulate metabolism and, therefore, potentially limit growth of stream biota. Howarth and Fisher (1976), Bothwell (1985, 1988), Peterson et al. (1983), Triska et al. (1983), Grimm and Fisher (1986), and Pringle (1987) used various combinations of these methods for determining growth, decomposition, or production responses to nutrient enrichment.

Artificial stream methods.—Because hydrodynamics influence a wide range of stream processes (Whitford and Schumaker 1961, Webster et al. 1975, Newbold et al. 1983a), conclusions based on laboratory and chamber studies must be evaluated within the context of flow before being extrapolated to whole streams. This evaluation is complicated by variability in flow regimes and other factors such as temperature, light, substratum, water chemistry. Artificial streams provide a simplified system for regulating certain hydrodynamic parameters. A uniform channel can minimize variability in velocity, turbulence, underflow, and dispersion associated with channel complexity. Conversely, limitations are thereby placed on the applicability of results to natural streams.

Investigations of processes influenced by flow can be approached from two basic perspectives. Flow can be made uniform for all experiments to focus on other processes of interest. Alternatively, flow can be manipulated so that its effect on a process can be evaluated. McIntire and Phinney (1965) used artificial streams to study community metabolism under controlled flow conditions, and McIntire (1966) investigated effects of current on metabolism. Similar studies could be performed to evaluate effects of flow on solute uptake. Gantzer et al. (1988) examined velocity effects on solute uptake in an artificial stream using a hydrodynamic model to link solute movement into biofilms with uptake kinetics occurring within the biofilm.

In addition to reduced complexity, in-stream flumes confine a small portion of total stream-flow and thereby facilitate manipulation and experimentation. Artificial streams or in-stream flumes have been used to examine uptake of nitrogen or phosphorus by periphyton (Triska

et al. 1983), and biotic and abiotic uptake of phosphorus (Mulholland et al. 1983, 1985a, Perkins et al. 1986, Munn 1989, D. J. D'Angelo and J. R. Webster, VPI&SU, unpublished data). Artificial streams can be used to assess the relative importance of biotic and abiotic processes because metabolic inhibitors can be added and then collected or diluted before discharge. In situ experiments using discrete, naturally isolated biotic patches such as bryophyte (Meyer 1979) or macrophyte (Crisp 1970) beds are analogous to single-pass flume methods because solute uptake of the biotic patch can be examined in isolation. Manipulations of animal density, which are difficult to perform in whole streams, can be done in artificial streams. This type of experiment allowed assessment of grazing effects on phosphorus spiralling (Mulholland et al. 1983, 1985a).

Experimental protocol

Experimental design.—An advantage of sub-system-level studies is that adequate controls and treatment replication permit full statistical analysis of data. Accurate estimates of sampling error and comparison of confidence intervals between data sets (Snedecor and Cochran 1967, Sudman 1976) depend on proper statistical replication and independence of experimental units.

Experimental conditions.—Solutes and microorganisms may bind to container walls due to physical, chemical, and biological mechanisms (Pringle and Fletcher 1986). The influence of this process increases with an increase in container surface area : volume ratio, and may vary with container composition (e.g., glass, metal, or plastic). Interactions between solutes and containers should be investigated experimentally or corrected for by use of control chambers.

Because retention primarily involves surface reactions, the surface area and composition of the streambed substrate must be considered. Identical weights of two sediment samples having a different particle size distribution might have drastically different surface areas, resulting in variable solute retention per unit weight among replicate treatments. Similarly, chemical and physical composition of sediment may significantly affect the sorption of both anions (Anderson and Malotky 1979) and cations (Davis 1984, Comans and Middelburg 1987). Other

factors that may significantly affect solute adsorption are: stream water pH and ionic strength (or conductivity); the presence of organics (both dissolved and particulate); and chemical speciation of the solute (Balistrieri and Murray 1982, Davis 1984, Kuwabara and Helliker 1988).

Expression of results.—The following physical and chemical variables are typically of interest and should be documented: 1) surface area and composition of sediment; 2) stream discharge and current velocity; 3) dimensions of the microcosm or stream reach; 4) experiment duration; 5) background solute concentration; 6) stream water pH, conductivity, and DOC concentration; and 7) solute concentration both initially and through time. For enclosure studies, documenting water volume and sediment (or biota) mass or surface area within the chamber is recommended. If experiments involve photoreactive solutes (e.g., Fe, Mn, and trace organics), light intensity measurements are suggested.

Scaling from microcosms to streams

Results of experiments conducted at small scales such as in situ chambers may be scaled up to larger systems by use of model equations. For example, a recirculating flume experiment may assess uptake of a radioactive tracer or of an added solute (Cummins et al. 1972, Dahm 1981, McDowell 1985, Corning et al. 1989, Paul et al. 1989). In such cases, the initial concentration decline may appear first order so that an uptake rate, k_c , may be calculated from the slope of a logarithmic plot. The value of k_c , however, depends on the ratio of sediments to water in the microcosm and cannot be applied to a stream without scaling correction. In some cases, it may be possible to duplicate the surface-to-volume ratio of the stream through microcosm design (Paul et al. 1989), but this may be impractical. We offer two approaches to reporting a scale-free rate of uptake, depending on design and assumptions of the microcosm experiment. First, if the microcosm is designed to mimic stream conditions at the sediment/water interface, and the process of interest is uptake across a unit area of stream bottom, then the mass transfer coefficient, v_t , is the appropriate scale-free variable. From Equation 9, $v_t = hk_c$, in which h is the effective depth of the microcosm, i.e., microcosm volume/area of stream sediments. An

equivalent value for k_c applicable to the stream can thus be obtained by dividing v_t by the stream depth h . Second, if the microcosm experiment is designed to mimic uptake on the basis of sediment mass, then the appropriate scale-free variable is k_{c_M} , in which ρ_M is the mass of sediments per unit volume of water in the microcosm. This variable has units of volume mass⁻¹ time⁻¹, and could be substituted for the term of the form $\lambda_s K_{ds}$ or $\lambda_B K_{dB}$ in Equation 6 in simulating whole stream dynamics.

Spatial and Temporal Scales in Solute Dynamics

Solute dynamics studies must recognize patterns of both physical characteristics and biological communities of streams and their valleys. Application of specific techniques may be restricted to limited spatial scales, flow conditions, or time intervals. Extrapolation of results to whole streams, catchments, or entire drainages requires hierarchically related concepts of landforms and biological communities. Similarly, comparison of solute dynamics over differing time frames within an annual cycle or between years must address temporal patterns of biological activity and the physical factors that influence that activity.

Geomorphic perspective on scaling

Hierarchical concepts of valley floor landscapes allow local patterns of solute dynamics to be interpreted or integrated at a basin scale (Frissell et al. 1986, Gregory et al., in press). In narrow, physically constrained reaches, for example, few geomorphic surfaces are possible, leading to simple plant community and channel structure. Hydraulic residence time of water is reduced and interactions with terrestrial ecosystems are limited. As a result, retention of solutes could be minimized. In contrast, broad, unconstrained reaches are characterized by long hydraulic resident times, major accumulations of stored sediments, and extensive subsurface flow. Retention of solutes may be physically and biologically enhanced in such reaches.

Analysis of geomorphic structure of drainages that encompass experimental stream reaches enhances the interpretation of individual experiments and provides a basis for extrapolation of results to longer stream reaches or to wa-

tersheds. Representative sequences of channel types such as constrained reaches and unconstrained reaches can be sampled in various valley landforms. The extent and distribution of these geomorphic features of a drainage basin serves as the basis for scaling the results of experiments to the entire drainage.

Biological perspective on scaling

Patterns of biological communities may strongly alter solute dynamics at all spatial scales. For example, although geomorphic processes dominate mechanisms of patch formation at larger spatial scales (Frissell et al. 1986, Gregory et al., in press), microhabitat patches are often formed by seasonal plant growth, leaf fall, or grazing activity. Foraging activities of grazers create patchiness in periphyton distributions on individual rocks (Hart 1981). Selective feeding on fungal assemblages maintains patchiness on decomposing leaves (Arsuffi and Suberkropp 1985). Tubes, cases, and retreats of relatively sessile organisms represent nutrient-rich, organic microenvironments that are clearly important in solute dynamics (Pringle 1985, Hershey et al. 1988). Biota can alter patterns of streamflow and create patches on a slightly larger scale as well. Macrophyte growth alters patterns of hyporheic-surface interchange (Hendricks and White 1988), and successional change in algal patch structure in desert streams results in distinct mesohabitats with characteristic physical and chemical features (Fisher et al. 1982, Grimm and Fisher 1989).

Modeling perspective on scaling and stream size

An important aspect of scaling involves comparing streams of different sizes and effects of parameters such as discharge, channel dimensions, and velocity on solute dynamics. The primary objective in this comparison may be to adjust for influences of scale, focusing on the similarity of solute exchange processes. In these cases, estimates of solute exchange rates per unit area or mass of stream sediment, organic matter, or algal or microbial biomass may serve well. As discussed previously, such estimates can be obtained by fitting a transport model to data obtained from a solute injection.

From the perspective of the whole stream or

drainage basin, however, the primary objective may be to characterize explicitly the influence of size on large-scale aspects of solute dynamics. This type of question can be investigated via model simulations by altering the hydrologic parameters, provided that two caveats are kept in mind. First, the hydrologic parameters do not vary independently of one another. To investigate the effects of increasing discharge, for example, one should also make appropriate alterations in the cross sectional characteristics. Second, this approach yields only the direct scaling effects of hydrologic parameters and should not be construed as a full description of the effects of altering stream size on nutrient dynamics. For example, the potential effect of increasing channel width on light availability, with consequent effects on algal growth and nutrient demand, is clearly not included in this type of analysis.

Although detailed questions concerning scaling would require specific application of model simulations, an approximate description of the effects of stream size on spatial and temporal scales can be obtained directly from the model equations and spiralling concepts presented previously. The uptake length, S_w , was defined as the average distance that a dissolved atom travels before being taken up and we showed that under certain assumptions, S_w defines the longitudinal rate of exponential decline of the plateau concentration of an injected solute. That is,

$$C(x) = C_0 e^{-x/S_w} \quad (13)$$

which is obtained by substituting the relation for S_w given in Equation 9 into Equation 10. Therefore, we suggest that uptake length indicates the longitudinal scale of solute dynamics in a stream. Similarly, the turnover time ($1/k_c$) is an index of the temporal scale of solute dynamics. These scaling indices are influenced by both transport and exchange processes, and their relation to stream model parameters is given by Equation 9. As Equation 9 shows, the uptake length, S_w , varies with stream size in direct proportion to the product of depth and velocity (uh), while turnover time, $1/k_c$, varies in direct proportion to depth (h) alone.

These basic scaling relations can be used to predict various effects of stream size on solute dynamics. Typical relations for downstream increases in depth and velocity are given by $h \sim$

$Q^{0.4}$ and $u \sim Q^{0.1}$ (Leopold et al. 1964). Thus, if processes governing exchange across the sediment water interface (in this case, the parameter v_i) are held constant, uptake length may be expected to increase approximately as the square-root of discharge, i.e., $S_w \sim Q^{0.5}$, with most of this increase attributable to increases in depth and relatively little to increases in velocity. In a comparison of two streams differing in flow by a factor of 100 (e.g., a first-order tributary and a third-order channel in the same catchment), the expected difference in uptake length would be about ten-fold and the difference in water column turnover time would be about six-fold. Although both streams have (by assumption) an identical ability to retain nutrients on a unit area basis, the smaller stream might be considered far more retentive per unit length in that any added nutrient is sequestered more quickly and within a much smaller distance.

As a second example, a comparison might involve two streams with similar flow but differing channel characteristics. Because flow is the product of velocity, depth, and width ($Q = uhw$), Equation 9 indicates that uptake length should vary inversely with width (i.e., $S_w \sim uh = Q/w$). Alterations of depth and velocity under a constant width would not affect uptake length, but would affect the turnover time of nutrients in the water column. Thus, as a stream flows into a reach affected by a beaver dam, or from a constrained reach into an unconstrained reach, nutrient retentiveness measured on a longitudinal scale increases as the channel widens. Again, it must be emphasized that these are not predictions of the full effects of altering stream size or shape. Rather, they isolate effects purely attributable to hydrologic alterations from many other effects that such alterations might have on nutrient retentiveness. Because hydrologic parameters may vary by several orders of magnitude over a range of stream sizes, they are likely to dominate many comparisons of nutrient retentiveness in streams of different sizes.

Summary

An initial workshop goal was to establish common methodological approaches for stream solute studies, particularly with respect to whole-stream solute injections. This commonality would facilitate comparisons of results be-

tween sites, especially for those investigators not able to utilize radiotracers. As the workshop progressed, it became evident that there were differences in conceptual approaches to these studies, in addition to methodological differences. As a result of this realization, the workshop focused on the integration of physical, chemical, and biological sciences to provide a common conceptual framework, particularly through the use of models.

The models presented in Equations 2, 4, and 6 present a simplified (one-dimensional) description of solute advection, dispersion, groundwater and tributary inputs, transient storage zones, and biotic and abiotic solute transfers. Even if an investigator does not attempt to fully simulate solute dynamics in a particular system using these or related models, recognition of model components can serve as focal points for individual studies. Applicability of the model equations is further demonstrated by their use as a scaling tool for experiments conducted at different scales and in different ecosystems. Simplification to a one-dimensional model can clearly be a limitation, however, if processes that operate cross sectionally or vertically are of potential importance.

An additional conclusion of the workshop was that no common methodological approach can serve every investigation of solute dynamics. Instead, more attention was paid to issues that affect experimental protocol and expression of results so that comparison of data between studies, particularly at different scales, can be facilitated. The major experimental approaches to stream solute studies were categorized as laboratory, chamber, flume, and whole-stream, representing a continuum from greatest control and least realism to least control and greatest realism. Where replication is of importance, process-level investigations are best conducted in an environment where the investigator has the greatest control over experimental conditions. Where field extrapolations are desired, environmental control may have to be sacrificed. Whole-stream processes are best addressed by studies of reaches to entire streams, with the recognition that hierarchically related concepts of landforms and biological communities can be used to scale up results to catchments and entire drainages.

We envision an increase in studies on stream

solute dynamics, ranging from specific processes responsible for solute retention to drainage-wide patterns of solute dynamics placed in the perspective of stream valley landforms. Major areas identified as requiring more attention include the use of biological inhibitors and uptake kinetics to elucidate the relative importance of biotic and abiotic mechanisms of retention, the relation between streambed patch characteristics and solute retention, sub-surface patterns of solute transport and transfer, the appreciation of biofilms in studies of biotic solute uptake, the importance of recycling within stream sediments and epilithic mats in meeting the nutrient demand of attached organisms, inter-biome comparisons of solute dynamics, integration of geomorphic perspectives into solute studies, and the use of solute transport and transfer models to compare results between studies of different scale. It is our hope that this paper can serve as a stimulus for such studies.

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