

7: Cycles and Spirals of Nutrients

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7.1 INTRODUCTION

Rivers play a major role in global biogeochemical cycling by transporting elements from terrestrial environments to the sea (Walling & Webb 1994). Many of these elements are essential nutrients and are utilized by river biota. A number of the major ions found in river water, such as Ca, Mg, K, Na, Si and Cl, are often present well in excess of any biological demands within the river, and may pass through the river system virtually unaffected. Other elements – notably, carbon, phosphorus and nitrogen, or particular chemical forms of these elements – may be in relatively short supply and undergo considerable utilization as they pass downstream.

Biota remove nutrients from river water, but they also regenerate nutrients to the water. This cycling of nutrients within the river may proceed intensively and yet produce small or negligible net effects on nutrient concentrations. In fact, for nutrients such as phosphorus, which does not exchange with the atmosphere, biota cannot alter the long-run total transport substantially. On the other hand, biota do influence the chemical and physical forms of nutrients, and the timing of nutrient transport. These effects may interact, in turn, with physical transport processes. For example, the biota might speed downstream transport by converting particulate-bound nutrients to dissolved forms or reducing detrital particles to smaller, more easily transported, sizes. Carbon, nitrogen and, to a limited extent, sulphur exchange with the atmosphere. For these elements, biota may strongly influence long-run total transport. This chapter considers the dynamics of selected chemicals (nutrients) *within*

river systems. For related reviews see Meyer *et al* (1988) and Stream Solute Workshop (1990).

Cycling is of interest not only because the biota may affect nutrient concentrations but because nutrient concentrations may affect the biota. These interactive influences, however, occur on a template of continual downstream transport, so that biotic processes in upstream reaches may influence those in downstream reaches. As a nutrient atom undergoes a series of transformations, completing a 'cycle' by returning to a previous state, it also traverses some distance downstream. This open, or longitudinally displaced, cycling has been termed 'spiralling' (Webster 1975; Wallace *et al* 1977; Webster & Patten 1979). Within the framework of the spiralling concept we can view cycling as involving exchanges and transformations that can be quantified on an areal or volumetric basis; it does not involve downstream transport (Fig. 7.1(a)). In this sense, cycling occurs at any point in the river, regardless of the fact that the atoms involved in the cycle represent an ever-changing population, and no individual atoms remain in place long enough to complete a cycle. Spiralling, on the other hand, involves measures of both cycling and downstream transport and refers explicitly to the longitudinal scale over which cycles occur (Fig. 7.1(b)).

7.2 OVERVIEW OF CYCLING AND SPIRALLING

Cycles

Figure 7.2 provides a simplified overview of the cycling of the three major elements we shall

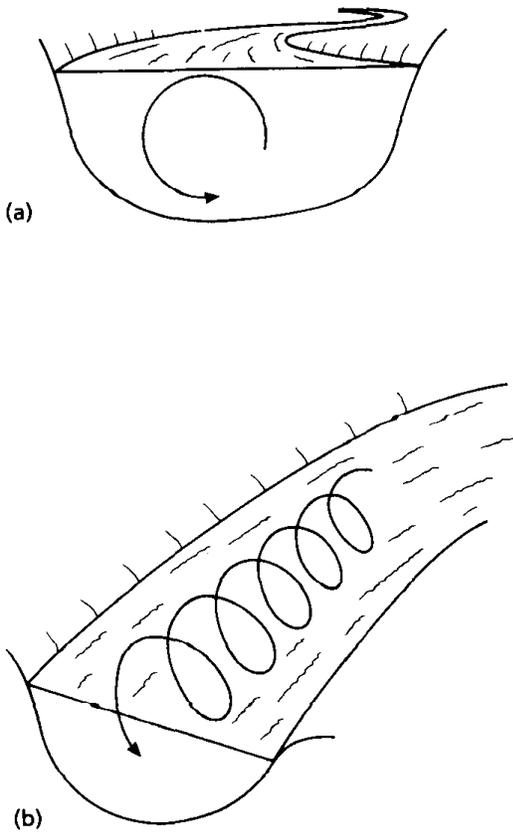


Fig. 7.1 (a) The nutrient cycle as viewed from a perspective that does not 'see' downstream transport. (b) The nutrient cycle, in conjunction with downstream transport, describes a spiral.

consider here: carbon, phosphorus and nitrogen. In this view of the river ecosystem, the metabolic activity within the river depends upon two major sources of organic carbon: primary production that occurs within the river (autochthonous carbon) and organic carbon supplied from the terrestrial environment (allochthonous carbon). Organic carbon passes through the food web (within which are significant subcycles not represented here) to an ultimate fate of being respired to dissolved inorganic carbon (DIC). Because DIC exchanges relatively freely with atmospheric carbon dioxide, we represent here only the organic-carbon 'half-cycle', which represents the primary pathway of energy flow in the ecosystem. The base of the carbon food web consists of both primary producers (algae, cyanobacteria, macrophytes, bryophytes; see Reynolds (1994), Fox (1994) and Wetzel & Ward (1994)), and microbial consumers of the allochthonous carbon (bacteria and fungi; see Maltby, 1994). Both groups use inorganic phosphorus and nitrogen from the river water, and these elements flow through the food web in rough stoichiometric proportion to the flow of carbon and energy. As the carbon is respired to DIC, the phosphorus and nitrogen are regenerated as inorganic forms to be recycled to the algae and microbes.

In many ecosystems, a large fraction of the metabolism is supported by recycled nutrient (Pomeroy 1970), i.e. total nutrient utilization

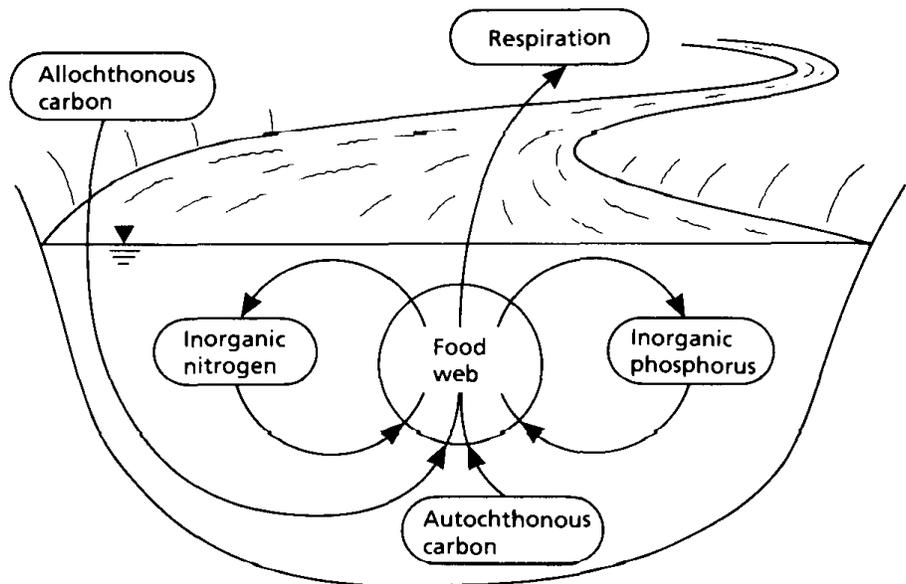


Fig. 7.2 Cycles of nitrogen and phosphorus are coupled to the 'half-cycle' of organic carbon.

within the ecosystem exceeds the supply of new nutrient from outside the ecosystem (Dugdale & Goering 1967). By delineating ecosystem boundaries and comparing imports and exports of nutrients to internal storage and utilization, much can be inferred about the significance of nutrient cycling to the productivity of the ecosystem. How does this logic apply to a stream or river? If the 'ecosystem' is a very short river reach, upstream imports and downstream exports may overwhelm internal utilization, suggesting that cycling is unimportant. Yet if the reach is very long, the opposite might be the case. To address these issues, we turn to the spiralling concept.

Spirals

A given nutrient atom, as it passes downstream, may be used again and again, the amount of utilization depending on the 'tightness' of the spirals (Webster & Patten 1979) or the downstream displacement from one cycle to the next. This in turn depends not only on how quickly cycling occurs, but also on the retentiveness of the ecosystem, or the degree to which the downstream transport of nutrient is retarded relative to that of water. That is, if it takes an average time, t_C , for the average nutrient atom to complete a cycle, while it moves downstream at an average velocity, v_T , then the cycle is completed over a downstream distance of:

$$S = v_T t_C \quad (1)$$

where S is the spiralling length (Elwood *et al* 1983). The velocity, v_T , may be near that of water, v_w , in large rivers, but very much lower in streams and rivers where nutrients reside in the sediments for a high proportion of the time.

The cycle of a nutrient such as phosphorus or nitrogen can be thought of as consisting of two components: (1) the biological assimilation ('uptake') of dissolved inorganic nutrients from the water column; and (2) the subsequent biological processing and movement through the food web leading eventually to regeneration to the inorganic form (Fig. 7.3). Spiralling length consists of the average downstream distance travelled by a dissolved nutrient atom until uptake (the 'uptake length') plus the downstream distance travelled within the biota until regeneration (the 'turnover length'). To illustrate the relationship between spiralling length, nutrient fluxes and nutrient retentiveness, we shall simplify the river ecosystem to two compartments: water (W), by which we mean the inorganic nutrient dissolved in the water, and biota (B), by which we mean nutrient in living tissue.

Suppose that the biotic utilization of nutrients from the water compartment is U , expressed as mass per unit area per unit time ($M L^{-2} T^{-1}$), and the downstream flux of dissolved nutrient is F_w , as mass per unit width of river per unit time ($M L^{-1} T^{-1}$), which can also be expressed as $F_w = C_w v_w d$, where C_w is the dissolved nutrient concentration, v_w is the water velocity, and d is river depth. Thus, in each unit distance of river, a

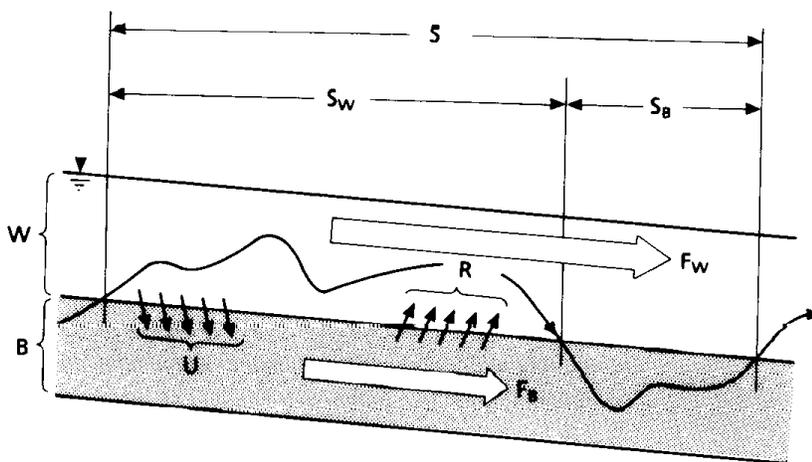


Fig. 7.3 Spiralling in a simplified river ecosystem consisting of two compartments: water (W) and biota (B). The spiralling length, S , is the average distance a nutrient atom travels downstream during one cycle through the water and biotic compartments. It is the sum of the uptake length (S_w) and the turnover length (S_b), and can be calculated from the downstream nutrient fluxes (F_w and F_b) and the exchange fluxes (U and R), as described in the text.

proportion, k_t (L^{-1}) = U/F_w , of the downstream flux is taken up by the biota. Depending on the level of nutrient regeneration and on external sources of nutrients, F_w may decline, remain uniform, or increase in the downstream direction. Provided, however, that the ratio U/F_w (i.e. k_t) remains uniform, then the particular atoms, F_w , passing any point in the river will disappear from the water column exponentially with distance, x :

$$F_w = F_{w0} \exp(-k_t x) \quad (2)$$

where $F_{w0} = F_w$ at $x = 0$. For example, if a tracer (such as $^{32}\text{PO}_4$ for phosphorus) is injected into a river, equation (2) describes the longitudinal disappearance of the tracer and can be used to estimate k_t (Ball & Hooper 1963; Newbold *et al* 1981). The average travel distance, or uptake length, is given by $S_w = 1/k_t$, which can be verified by a simple integration of equation (2). Thus, since $k_t = U/F_w$:

$$S_w = F_w/U \quad (3)$$

If followed downstream at the water velocity, v_w , the nutrient atoms disappear exponentially with time (as well as distance), at the rate $k_w = k_t v_w$. Substituting for k_t , we can write $S_w = 1/k_t = v_w/k_w$, or, given that the residence time in the water is $t_w = 1/k_w$, $S = v_w t_w$. The stock of inorganic nutrient, on a unit-area basis, is $X_w = C_w d$, so that the uptake can be written as $U = k_w X_w$.

The turnover length, or distance of travel in the biotic compartment, is analogous to the uptake length. Suppose that the standing stock of nutrient in the biota is X_b [$M L^{-2}$], and that a fraction, k_b , is regenerated per unit time giving a residence time for nutrient atom of $1/k_b$, and a regeneration flux of R [$M L^{-2} T^{-1}$] = $k_b X_b$. The biotic compartment is distributed between that in the water column X_{sus} (moving downstream at v_w) and that in the sediments, X_{sed} (with zero velocity). That is, $X_b = X_{sus} + X_{sed}$. The weighted average velocity at which the compartment as a whole moves downstream, then is $v_b = (X_{sus}/X_b)v_w$. Therefore, during its residence time of $1/k_b$ in the biotic compartment, a nutrient atom will travel an average distance:

$$S_b = v_b/k_b \quad (4)$$

which is the turnover length.

The downstream flux (per unit width) of the biotic compartment is F_b [$M L^{-1} T^{-1}$] = $v_w X_{sus} = v_b X_b$. From this, and the definition of R above, it can be seen that equation (4) is equivalent to:

$$S_b = F_b/R \quad (5)$$

The total downstream displacement during one cycle, or spiralling length, then is:

$$S = S_w + S_b = v_w/k_w + v_b/k_b = F_w/U + F_b/R \quad (6)$$

In the idealized case in which the river is at steady state and is longitudinally uniform on the scale of the spiralling length, the regeneration flux equals the uptake flux ($R = U$) so that:

$$S = F_t/U \quad (7)$$

where F_t is the total downstream nutrient flux, or $F_w + F_b$. Thus, the spiralling length represents the distance of river over which utilization is equal to the downstream flux of nutrients or, alternatively, over which the downstream flux is cycled, on average, only once.

Equation (7) quantifies the intuitive idea that more intensive nutrient utilization involves cycling over shorter distances, or 'tighter' spiralling. The total time for completing a cycle is $t_c = 1/k_w + 1/k_b$, while the average downstream velocity for the entire nutrient stock is, $v_t = F_t/X_t$, where $X_t = X_w + X_b$. By combining these definitions with equation (6) and assuming $R = U$, one can obtain equation (1), i.e. $S = v_t t_c$.

An actual analysis might involve several ecosystem compartments (see section 7.6). Each compartment has a turnover rate and a downstream velocity, and hence a turnover length. The total spiralling length can be determined from the individual turnover lengths by weighting each compartmental turnover length by the proportion of the total uptake flux that passes through it, and summing these weighted values (Newbold *et al* 1983a). The biotic compartment presented here, and its turnover length, may be thought of as an aggregation of the entire portion of the cycle in which the nutrient is not in the dissolved inorganic form, and hence is temporarily unavailable for plant and microbial uptake. This may include nutrient in dead tissue and nutrient in less available organic molecules. However, if the biotic compartment actually consists of several

compartments with differing turnover rates and transport velocities, the equation $S_n = F_n/R$ is only an approximation unless the ecosystem is at steady state and without longitudinal gradients in standing stock.

7.3 NUTRIENT LIMITATION AND NUTRIENT RETENTION

Primary productivity in most of the world's lakes is limited by phosphorus, nitrogen, or both, even when these nutrients are supplied at relatively high levels of anthropogenic enrichment (Dillon & Rigler 1974; Vollenweider 1976; Elser *et al* 1990). Nutrient limitation of primary productivity and microbial activity in streams and smaller rivers, however, appears to be far less widespread and largely restricted to near-pristine conditions. Phosphorus limitation of algal growth or production has been reported in several streams (Stockner & Shortreed 1978; Elwood *et al* 1981b; Horner & Welch 1981; Pringle & Bowers 1984; Bothwell 1985, 1988; Peterson *et al* 1985; Freeman 1986; Knorr & Fairchild 1987; Pringle 1987; Keithan *et al* 1988; Biggs & Close 1989; Hart & Robinson 1990; Horner *et al* 1990; Lock *et al* 1990), and there have been a few reports of phosphorus limitation of heterotrophic microbial activity (Elwood *et al* 1981b; Klotz 1985; Lock *et al* 1990). In all cases concentrations of soluble reactive phosphorus (SRP, see section 7.6) were $\leq 15 \mu\text{g l}^{-1}$ and frequently $< 5 \mu\text{g l}^{-1}$. Mixed results have been reported in the range of $3\text{--}50 \mu\text{g l}^{-1}$ (Wurhmann & Eichenberger 1975; Wong & Clark 1976; Horner & Welch 1981; Horner *et al* 1983; Bothwell 1985, 1989; Klotz 1985; Hullar & Vestal 1989), while higher concentrations have not revealed limitation (Pringle *et al* 1986; Knorr & Fairchild 1987; Keithan *et al* 1988; Munn *et al* 1989).

Periphyton growth has responded to nitrogen enrichment in several streams where inorganic nitrogen concentrations were less than $60 \mu\text{g l}^{-1}$ (Grimm & Fisher 1986; Hill & Knight 1988; Triska *et al* 1989a), and has failed to respond in streams where inorganic nitrogen exceeded $50 \mu\text{g l}^{-1}$ (Wurhmann & Eichenberger 1975; Pringle *et al* 1986; Knorr & Fairchild 1987; Keithan *et al* 1988; Munn *et al* 1989). The ap-

parently consistent transition at $50\text{--}60 \mu\text{g l}^{-1}$ should be viewed with caution because of the small number of studies involved, and because inorganic nitrogen includes both ammonium and nitrate, which are assimilated with differing efficiencies (see section 7.7). Meyer and Johnson (1983) inferred that microbial activity in decomposing leaves was nitrogen limited at $8 \mu\text{g l}^{-1}$, whereas Newbold *et al* (1983b) saw no effect at $30 \mu\text{g l}^{-1}$.

One explanation for the lower incidence of nutrient limitation in streams than in lakes is that water velocity and associated turbulence have an enriching effect (Ruttner 1963). Uptake of nutrients by periphyton is enhanced at higher velocities (Whitford & Schumacher 1961, 1964), presumably because diffusion barriers to nutrient transport are reduced. Yet this explanation is not sufficient because: (1) planktonic algae regularly deplete nutrients to levels far below those at which nutrient limitation has been observed in streams; and (2) algal mats or biofilms present a diffusion barrier that at least partially offsets the enriching effect of velocity (Bothwell 1989).

An alternative explanation for the lower incidence of nutrient limitation in streams is that they are open systems with a large capacity to retain nutrients. Lakes are vulnerable to nutrient limitation in large part because they act, in the short run, as closed systems. The total nutrient in the water column remains relatively constant but, as plankton populations increase, dissolved available nutrient is incorporated into biomass. Net incorporation of nutrient necessarily ceases when nearly all of the nutrient is sequestered. It is this very low residual concentration, rather than the potentially high initial concentration, that actually limits algal growth.

In a stream with a continual supply of nutrient from the watershed, benthic organisms may deplete the available nutrient supply in three ways: (1) by temporarily reducing downstream flux (F_T) during nutrient accumulation (Grimm 1987); this depletion ceases at steady state; (2) diverting nutrients to the atmosphere or terrestrial environment; this is rarely significant except for denitrification (section 7.7); and (3) detaching and carrying the nutrient downstream in unavailable form, i.e. as the flux, F_n . In the latter case, the

flux of dissolved inorganic nutrient at steady state is $F_w = F_T - F_R$. Recalling from the previous section that the total biomass X_R migrates downstream at the velocity v_R , and that $F_R = v_R X_R$, we see that nutrient depletion increases as the retentiveness of the stream or river decreases. A retentive stream is characterized by a short turnover length relative to the uptake length since, if $R = U$, equation (6) yields:

$$S_w/S_R = F_w/F_R \quad (8)$$

Many streams and smaller rivers are highly retentive ($v_R \ll v_w$), supporting large standing stocks with little nutrient depletion (Newbold *et al* 1982b; Newbold 1987; section 7.6). Thus, we would expect nutrient limitation to occur only as a transient phenomenon during rapid growth, or when nutrient is supplied from the watershed at concentrations already low enough to be limiting.

Growth rates of many algae and bacteria are saturated by nutrient concentrations substantially below the limiting concentrations observed in the field studies reviewed above. To explain this discrepancy, Bothwell (1989) suggested and experimentally supported the hypothesis that nutrient concentrations can be locally depleted to limiting levels within algal biofilms. A second possible explanation for the discrepancy—applicable to phosphorus limitation—is that soluble reactive phosphorus measurements may overestimate $\text{PO}_4\text{-P}$ concentrations (section 18.6).

In larger, less retentive, rivers we might expect nutrient depletion and nutrient limitation to be more prevalent. In an entirely planktonic river, where $v_R = v_w$, nutrient in biomass depletes the dissolved inorganic nutrient on a one-to-one basis, as in a closed algal culture or the epilimnion of a lake. River phytoplankton has been reported to deplete phosphorus from municipal discharges to limiting levels (Décamps *et al* 1984). But in several rivers, phytoplankton has been observed not to be nutrient limited (Burkholder-Crecco & Bachmann 1979; Megard 1981; Elser & Kimmel 1985; Krogstad & Løvstad 1989; Wiley *et al* 1990). Three factors—non-algal turbidity, extremely high nutrient concentrations and water residence time—seem to account for the absence of nutrient limitation. Søballe and Kimmel (1987), in a comparison of 126 rivers with 149 natural lakes in the

USA, found that in rivers with residence times (i.e. time-of-travel from the river source) greater than about 50 days, the relationship between total phosphorus and phytoplankton populations approximated that of lakes (strongly implying nutrient limitation), whereas in rivers with shorter residence times, phytoplankton populations were lower than in lakes with equivalent phosphorus concentrations.

7.4 MODELLING SPATIAL AND TEMPORAL VARIATION

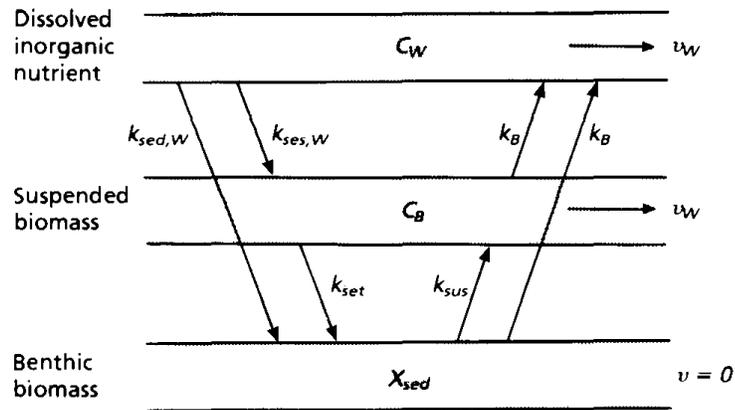
The spiralling concept as presented so far does not account for spatial and temporal variation in nutrient fluxes and stocks. Mathematical simulations are widely used to describe such variations, as well as other aspects of ecosystem dynamics in rivers. Many river models express the behaviour of the concentration, C , of a solute or suspensoid in the water column as a one-dimensional advection–dispersion equation, one form of which is:

$$\frac{\partial C}{\partial t} = \underbrace{\frac{-Q}{A} \frac{\partial C}{\partial x}}_{\text{Advection}} + \underbrace{\frac{1}{A} \frac{\partial}{\partial x} \left[AD \frac{\partial C}{\partial x} \right]}_{\text{Dispersion}} + \underbrace{\frac{\partial Q}{\partial x} (C_i - C)}_{\text{Inflow and dilution}} + \underbrace{N}_{\text{Net of sources and sinks}} \quad (9)$$

where x is downstream distance, Q is stream flow, A is cross-sectional area, D is the coefficient of longitudinal dispersion [$\text{L}^2 \text{T}^{-1}$], C_i is the concentration of influent water, and N [$\text{M L}^{-3} \text{T}^{-1}$] is the net of gains from all losses to other ecosystem compartments, the atmosphere, or the terrestrial environment.

Differences among models include the forms of the source and sink terms, whether the channel and flow characteristics can vary with space and time, the number of solutes and suspensoids that are modelled simultaneously, and the number of additional, non-transporting compartments that are coupled to the source and sink terms. Only the simplest forms have analytical solutions; most require numerical solution by computer.

Figure 7.4 presents a model for the simple



$$\frac{\partial C_W}{\partial t} = -v_W \frac{\partial C_W}{\partial x} + \frac{\partial}{\partial x} D \frac{\partial C_W}{\partial x} - k_W C_W + \frac{1}{d} k_B X_B$$

$$\frac{\partial C_B}{\partial t} = -v_W \frac{\partial C_B}{\partial x} + \frac{\partial}{\partial x} D \frac{\partial C_B}{\partial x} - (k_B + k_{set}) C_B + \frac{1}{d} k_{sus} X_{sed} + k_{ses, W} C_W$$

$$\frac{\partial X_{sed}}{\partial t} = - (k_B + k_{sus}) X_{sed} + d k_{set} C_B + d k_{sed, W} C_W$$

where

$$X_B = X_{sed} + dC_B$$

$$k_W = k_{ses, W} + k_{sed, W}$$

$$\text{Uptake length, } S_W = v_W/k_W$$

$$\text{Biomass transport velocity, } v_B = k_{sus}/(k_{set} + k_{sus})$$

$$\text{Turnover length, } S_B = v_B/k_B$$

two-compartment ecosystem used above to introduce spiralling. The biotic compartment is subdivided into a suspended portion and a sedimentary portion. The advection–diffusion equations are simplified, relative to equation (9), by assuming uniform flow and cross-section. The equation for the sediment compartment contains no transport terms and is expressed in terms of mass per unit area. As illustrated in Fig. 7.4, spiralling length can be computed from the model parameters.

An important aspect of this model is that all transfers among compartments vary linearly with the nutrient content of the donor compartment. A linear, donor-controlled model cannot incorporate many mechanisms known to control exchanges among compartments. It does not, for example, include an influence of biomass on nutrient uptake, or any means for saturating uptake at high nutrient concentrations. A model of this type is, however, appropriate for simulating the

Fig. 7.4 Linear, donor-controlled (or tracer) model for a two-compartment, longitudinally uniform, stream ecosystem.

dynamics of a tracer (such as a radioisotope) added to a stream or river in which other aspects of the ecosystem, including the cycling of the naturally occurring nutrient, are relatively constant (O'Neill 1979). This is because a tracer, by definition, is added at a level too low to affect the dynamics of naturally occurring nutrient or any other aspect of the ecosystem. The model, therefore, simulates only the simple mixing of the tracer through compartments at rates determined by the steady fluxes of the naturally occurring nutrient. Model coefficients estimated by simulating a tracer injection, therefore, quantify the cycling of the ecosystem under the conditions of the experiment, but may poorly predict responses to altered conditions, such as addition of polluting levels of a nutrient.

Where the objective is to describe or investigate the dynamics of nutrient concentration over a range of concentrations, such as might be pro-

duced by an experimental nutrient addition, non-linear functions may be used. For example, to model uptake by attached algae of nitrate added to experimental flumes, Kim *et al* (1990) used an additional water compartment with no downstream velocity representing an 'exchange zone' near the streambed. Nutrient transfer into the exchange zone from the water column was governed by first-order kinetics, while nutrient uptake occurred from the exchange zone according to Michaelis–Menten kinetics, i.e.:

$$U = X_B V_{\max} \left(\frac{C_{\text{ex}}}{K_s + C_{\text{ex}}} \right) \quad (10)$$

where C_{ex} is the $\text{NO}_3\text{-N}$ concentration in the exchange zone, K_s is the half-saturation constant at which uptake is half its maximum rate, V_{\max} [M T^{-1} per mass of X_B]. Note that equation (10) predicts that uptake length will increase with increasing concentrations, as has been observed experimentally by Mulholland *et al* (1990). In non-biological applications, other types of exchanges, such as sorption isotherms (Bencala 1984), and chemical submodels (Chapman 1982), have been coupled to equation (9). Functions used in modelling trace contaminant behaviour have been reviewed by Thomann (1984), Kuwabara and Helliker (1988), and O'Connor (1988a, 1988b, 1988c).

The dynamics of an added nutrient, unlike those of a tracer, may interact with other aspects of the ecosystem. For example, using equation (10) to describe an increase in uptake due to added nutrients raises the question of whether the biomass, X_B , increases in response. This, in turn, may depend on whether there is a secondary effect on consumer populations that might keep X_B in check (section 7.8). Considerations such as these lead to increasingly complex ecosystem models in which the dynamics of a single nutrient are only a small part.

Such complexity appears, to varying degrees, in water quality simulation models, designed to predict effects of potential waste discharges, or of reducing existing discharges (Chapra & Reckhow 1983; Orlob 1983; Bowie *et al* 1985; Thomann & Mueller 1987; McCutcheon 1989). Several water quality models simulate phosphorus and nitrogen dynamics, including release of these nutrients

from discharged organic matter, uptake by and influence on the growth of algae, releases from decaying algae, and exchanges with sediments. Often, however, the focus is on the net effects on water-column concentrations, rather than on cycling *per se*, and in some models the sediments are regarded as potentially infinite sources or sinks without mass balance constraints. Water quality simulation models are typically constructed by using functional relationships and parameter values available in the scientific literature (see Bowie *et al* 1985) and then adjusted to bring model simulations into agreement with data from a particular river. These data are often limited, either in quantity or in dynamic range, so that unequivocal parameter estimations and rigorous testing of the model are rarely feasible. None the less, the models are undeniably effective in simulating major water quality parameters, and they serve to identify areas in which scientific understanding of ecosystem processes is limited.

7.5 ORGANIC CARBON SPIRALLING

The carbon cycle in rivers differs from that of phosphorus and nitrogen in that: (1) the inorganic phase of the cycle (CO_2 , HCO_3^- , and CO_3^{2-}) exchanges freely with atmospheric carbon dioxide; and (2) a variable, but sometimes very large, proportion of the organic phase begins not with uptake of inorganic carbon (i.e. photosynthesis), but with lateral accrual of organic carbon from the terrestrial environment. In describing spiralling of carbon, therefore, we focus on the portion of the cycle, or half-cycle, involving organic carbon, beginning with its entry into the river from terrestrial sources or formation by photosynthesis and ending in respiration to carbon dioxide. The organic matter turnover length, S_c , is the expected downstream travel distance associated with this half-cycle (Newbold *et al* 1982a). As we shall see below, both computation and meaningful interpretation of S_c are made problematic by the very great diversity of organic carbon forms in a river.

For the moment, however, we assume that all organic carbon in the river is of similar quality, degrading at the rate k_c , and migrating down-

stream at the velocity, v_c . The turnover length, then (as derived above), is $S_c = v_c/k_c$. If X_c is the areal standing stock of organic carbon (hereafter 'carbon'), then the areal rate of carbon loss to respiration is $R = k_c X_c$, and the downstream flux of carbon per unit width is $F_T = v_c X_c$. Simple substitutions yield:

$$S_c = F_T/R_w \quad (11)$$

This allows turnover length to be estimated from measurements of downstream transport and areal respiration in the river. S_c , like spiralling length, measures the combined effects of retentiveness (v_c) and rate of biological processing (k_c) in determining how effectively a unit of river bottom processes nutrient supplied from upstream. Moreover, under our simplifying assumption of uniform carbon quality, the turnover length describes how carbon entering the river at a particular location affects downstream metabolism. For example, if I^* is a steady input (per unit area) to a unit length of river at location $x=0$, then the respiration $R^*(x)$ at downstream distance x attributable to I^* is given by $R^* = (I^*/S_c) \exp(-x/S_c)$. This is essentially the same model that Streeter and Phelps (1925) used to describe the downstream effects of organic matter in sewage effluent. Streeter and Phelps assumed that all organic matter remained in suspension ($v_c = v_w$), expressed R in terms of oxygen utilization, and coupled this model with one describing oxygen depletion and re-aeration. The Streeter-Phelps approach, although sometimes highly elaborate, remains the basis for many currently used water quality models (Gromiec *et al* 1983; *cf.* section 7.4).

Estimates of organic carbon turnover length, based on equation (11), have been made for several streams and rivers (Newbold *et al* 1982a; Minshall *et al* 1983, 1992; Edwards & Meyer 1987; Naiman *et al* 1987; Meyer & Edwards 1990; Richey *et al* 1990). Values ranged from 2.9 km for a small wooded stream in New Hampshire, USA (data from Fisher & Likens 1973), to 4000 km for the Amazon River (Richey *et al* 1990). Minshall *et al* (1983) estimated the turnover lengths of only particulate carbon (i.e. excluding dissolved organic matter). Their estimates ranged from 1.0 to 10 km in headwater North American streams

to 250 km in the McKenzie River, Oregon, with an average flow of $55 \text{ m}^3 \text{ s}^{-1}$ (Minshall *et al* 1983). The major influence on turnover length is stream size. Areal respiration often, but not always, increases in the downstream direction, and the variation usually remains within one order of magnitude (Minshall *et al* 1983, 1992; Bott *et al* 1985; Naiman *et al* 1987; Meyer & Edwards 1990). Water-column organic matter concentration may increase somewhat with stream size but on the whole remains remarkably constant (Schlessinger & McLack 1981; Mulholland & Watts 1982). It is, therefore, the simple variation in depth and velocity that accounts for most of the size effect on turnover length (since $F_T = v_w dC_c$, where C_c is total organic carbon concentration).

Carbon turnover lengths are generally longer than the stream or river in which they were measured. That is, most of the carbon entering a river is transported, either to a larger downstream river or to an estuary or sea. Much of the carbon reaching the sea is highly refractory (Ittekkot 1988), and probably undergoes very little degradation within the river system. Clearly, much of the metabolism in a river is of more labile forms, such as algae and fresh leaf litter, which contribute little to transport. This diversity of forms affects the estimation of turnover length. Equation (11), in effect, yields an average of the individual turnover of the various forms of carbon, weighted by their relative contribution to the measured respiration. Respiration of forms whose turnover length is short relative to river length can be expected to be about equal to the rate of lateral input (on an annual basis), while respiration of forms with very long turnover lengths must be far less than lateral inputs. Thus, a turnover length weighted by carbon inputs rather than by respiration would be much longer than estimated by equation (11).

The promise of analysing organic carbon dynamics from the perspective of spiralling is that it might provide a measure of the upstream-downstream interdependence of the river ecosystem. Such a measure would be useful from a practical standpoint, for example in evaluating the importance of protecting headwater stream reaches to maintain a downstream fishery. It

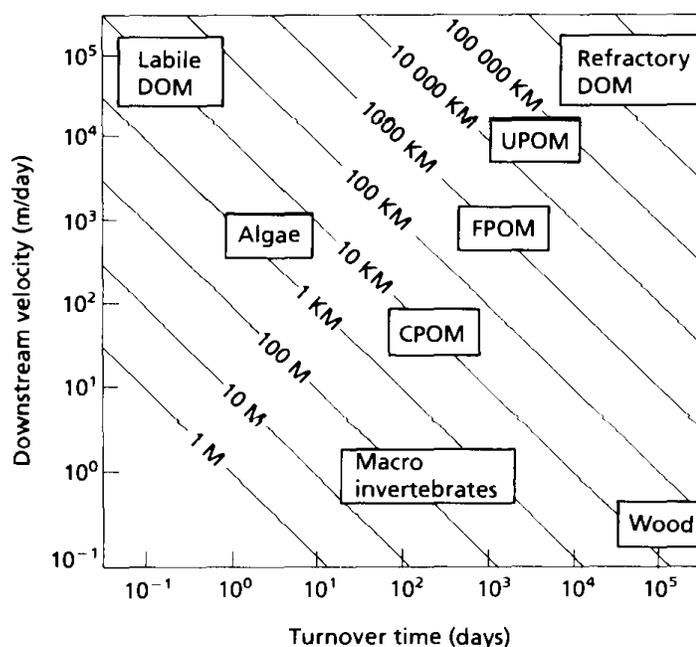


Fig. 7.5 Postulated turnover lengths (diagonal isoclines) for carbon of various forms in a medium-size river (e.g. with a flow of $3\text{--}30\text{ m}^3\text{ s}^{-1}$). Values represent rough averages from various sources and some speculation. Data sources include: Waters 1961, 1965; Fisher 1977; Marker & Gunn 1977; Minshall *et al* 1983, 1992; Bott *et al* 1985; Webster & Benfield 1986. CPOM, coarse particulate organic matter ($>1\text{ mm}$); FPOM, fine particulate organic matter ($50\text{ }\mu\text{m}$ to 1 mm); UPOM, ultrafine particulate organic matter ($<50\text{ }\mu\text{m}$); DOM, dissolved organic matter.

would also provide an approach to analysing longitudinal variations in ecosystem structure, such as those postulated by the river continuum concept (Vannote *et al* 1980). If natural carbon were uniform in character, the turnover length, in conjunction with the simple exponential decay model presented above, would provide such a measure as it does for the case of organic pollution. But the diversity of organic carbon prevents this interpretation. If, for example, a turnover length of 100 km is an average of two kinds of carbon with turnover lengths of 1 km and 199 km , respectively, the turnover length tells us little about the longitudinal interdependence of the river ecosystem. What is necessary, is to describe carbon spiralling in terms of specific carbon forms, accounting not only for the individual turnover lengths of these forms, but for the transformation of carbon among them.

Such an analysis has not been conducted, but sufficient information exists to illustrate its potential. Figure 7.5 presents rough turnover times ($1/k_c$) and downstream transport velocities (v_c) for a small river (e.g. baseflow $3\text{--}30\text{ m}^3\text{ s}^{-1}$), representing a composite of several studies. Turnover lengths for the individual forms range over approximately eight orders of magnitude from $\sim 100\text{ m}$ for macroinvertebrates to $\sim 10^6\text{ km}$ or more for refractory dissolved organic matter. Note

that labile DOM and woody debris, which occupy opposite extremes on the turnover time and velocity axes, both have intermediate turnover lengths in the range of $10^2\text{--}10^4\text{ m}$. The downstream influence of carbon of a given form depends not only on the turnover length shown here, but also on its conversion to other forms. For example, carbon initially in algae and coarse particulate organic matter (CPOM) may remain local if assimilated by macroinvertebrates, but pass downstream if it is leached as labile DOM or converted to fine particles (FPOM). In rivers of larger or smaller size, we would expect turnover times to remain roughly as in Fig. 7.5, but downstream velocities would differ dramatically. Transport velocities of CPOM, and FPOM in first-order streams, for example, are of the order of 0.1 and $1\text{--}10\text{ m day}^{-1}$, respectively.

Figure 7.5 suggests that longitudinal linkages — or influences of upstream ecosystems on downstream ecosystems — may be transmitted primarily through labile DOM, algae, CPOM, FPOM, and wood; that is, the forms whose turnover lengths are on the scale of the river length. In contrast, most of the downstream transport of carbon in unpolluted streams and rivers occurs as refractory DOM and particles smaller than $50\text{ }\mu\text{m}$ (UPOM) (Wallace *et al* 1982; Minshall *et al* 1983), which are forms with extremely long turnover

lengths. A complete analysis will require coupling the turnover-length concept with budgetary studies of individual reaches (e.g. Fisher & Likens 1973; Fisher 1977; Mulholland 1981; Cummins *et al* 1983; Richey *et al* 1990), and with geomorphic approaches which consider the role of all channels, of all sizes, within a river network (e.g. Cummins *et al* 1983; Naiman *et al* 1987; Meyer & Edwards 1990).

7.6 PHOSPHORUS

Forms and concentrations

Phosphorus is an essential nutrient centrally involved in energy transformations within organisms, making up roughly 0.1–1% of organic matter. Figure 7.6 illustrates the major aspects of the phosphorus cycle in rivers. Phosphorus in water is normally categorized as being either dissolved or particulate, depending on whether it passes 0.45- μm membrane filter. 'Dissolved' phosphorus, therefore, may include a substantial colloidal component. Within the dissolved fraction, inorganic P (DIP) occurs as orthophosphate (PO_4), which is usually estimated by variations of the molybdenum blue method (Strickland & Parsons 1972). Because this method may overestimate the orthophosphate by hy-

drolysing organic and colloiddally bound forms (Rigler 1966; Stainton 1980; Tarapchak 1983), measurements based on the molybdenum blue method are often referred to as 'soluble reactive phosphorus' (SRP). 'Total dissolved phosphorus' (TDP) represents a molybdenum blue assay for phosphorus following an acid digestion that releases the dissolved phosphorus in organic forms. The organic fraction (DOP) is not well characterized, but in lake water some consists of inositol hexaphosphate (Herbes *et al* 1975; Eisenreich & Armstrong 1977) and DNA fragments (Minear 1972).

In unpolluted rivers, SRP averages about $10 \mu\text{g l}^{-1}$ (Meybeck 1982) on a worldwide basis, while total dissolved phosphorus averages about $25 \mu\text{g l}^{-1}$. Dissolved phosphorus concentrations may increase with discharge, but rarely by a factor of more than 2–4 during peak flows (Kunishi *et al* 1972; Leonard *et al* 1979; Meyer & Likens 1979; Saunders & Lewis 1988). Agricultural activities may increase dissolved phosphorus to the range of $50\text{--}100 \mu\text{g l}^{-1}$ (Omernik 1977; Smart *et al* 1985; Mason *et al* 1990), and to $>500 \mu\text{g l}^{-1}$ during snowmelt (Rekolainen 1989). Municipal effluents, however, may increase concentrations to the range of $1000 \mu\text{g l}^{-1}$ (Meybeck 1982).

Particulate phosphorus includes phosphorus

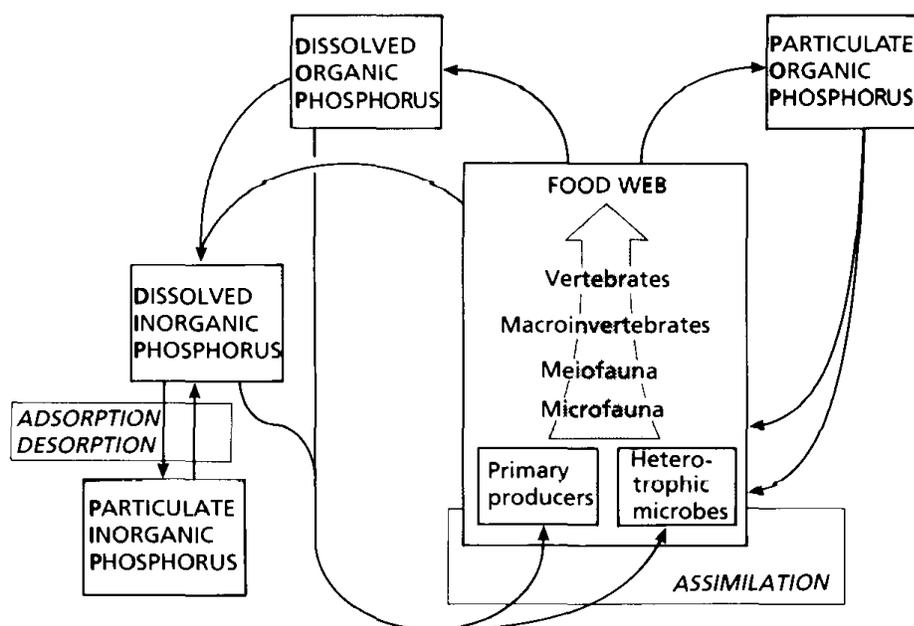


Fig. 7.6 Schematic of the phosphorus cycle in streams and rivers.

incorporated into mineral structures, adsorbed on to surfaces, primarily of clays, and incorporated into organic matter, and averages worldwide about $500 \mu\text{g l}^{-1}$ (Meybeck 1982). Concentrations of suspended particulates vary greatly with land use and erodibility of the watershed (Cosser 1989; Karlsson & Löwgren 1990) and increase dramatically with stormflows (Kunishi *et al* 1972; Verhoff & Melfi 1978; Meyer & Likens 1979; Munn & Prepas 1986; Prairie & Kalff 1988; Krogstad & Løvstad 1989).

Dissolved-to-particulate transfers

Movement from the dissolved inorganic (DIP) compartment to other ecosystem compartments is perhaps best observed by adding a radioisotope tracer, $^{33}\text{P-PO}_4$, directly to a stream river. Unfortunately, this is not generally feasible, and such experiments have been conducted in only a few streams and one relatively small river. The uptake length can be estimated from equation (2) and the longitudinal disappearance of ^{32}P relative to a hydrological tracer such as $^3\text{H-H}_2\text{O}$ or chloride. In Walker Branch, a first-order woodland stream in Tennessee, USA (baseflow $3\text{--}8 \text{ l s}^{-1}$), ^{32}P -estimated uptake lengths ranged from 21 to 165 m, varying roughly inversely with the quantity of leaf detritus on the stream bottom (Mulholland *et al* 1985b). Corresponding rates of phosphorus uptake were $1.8\text{--}22 \text{ mg}^{-2} \text{ day}^{-1}$. In the Sturgeon River, Michigan, USA, with a flow increasing downstream from 1.1 to $1.4 \text{ m}^3 \text{ s}^{-1}$, Ball and Hooper (1963) estimated uptake lengths between 1100 and 1700 m in successive reaches (with no downstream trend). From their data, areal uptake of phosphorus averaged about $10 \text{ mg}^{-2} \text{ day}$, or near the middle of the range of estimates from Walker Branch.

Chambers, or microcosms, offer a promising but underexploited alternative method for using ^{32}P to estimate phosphorus uptake (Corning *et al* 1989; Paul *et al* 1989; Paul & Duthie 1989; Stream Solute Workshop 1990). Corning *et al* (1989) incubated rocks from Canadian streams and rivers under *in situ* conditions of temperature and flow in closed 6-litre recirculating chambers. Initial loss of ^{32}P from solution is first order until regeneration of ^{32}P becomes significant. Corning

et al reported uptake rates by the epilithon ranging from 0.5 to $4.3 \text{ mg m}^{-2} \text{ day}^{-1}$.

Estimates of phosphorus removal based on tracer data may be erroneously high if the true levels of PO_4 are below the value estimated as SRP. This problem has proved particularly vexing in lakes, where SRP may overestimate PO_4 by more than an order of magnitude (Rigler 1966; White *et al* 1981). Peters (1981), using a radiological bioassay, found that PO_4 constituted between 6% and 44% of SRP in water from various river waters, but the radiobiological method (based on Rigler 1966) has been criticized by Tarapchak and Herche (1988). Jordan and Dinsmore (1985), also using radiobioassay, concluded that in the River Main in Northern Ireland the readily available phosphorus (presumably PO_4) accounted for 76% of the SRP. Newbold *et al* (1983a) inferred from exchange rates with periphyton of known pool size, that true PO_4 concentrations in Walker Branch were at least 70% of the average SRP.

Several studies have observed the uptake of stable phosphorus (^{31}P) experimentally injected into small streams (McCull 1974; Meyer 1979; Aumen *et al* 1990; Mulholland *et al* 1990; Munn & Meyer 1990; D'Angelo *et al* 1991). In a few cases, the observed net uptake of phosphorus has been negligible, indicating that whatever uptake occurs in the stream is saturated at ambient phosphorus concentrations. In most cases, however, considerable retention of the added phosphorus occurred, with uptake lengths in the range of 5–200 m. An uptake length measured by adding stable phosphorus is equivalent to one measured using ^{32}P only if the uptake flux of phosphorus increases in direct proportion to the increase in concentration (i.e. F/U remains constant). Mulholland *et al* (1990) found that an addition which increased PO_4 concentration from a background of $2.9 \mu\text{g l}^{-1}$ to $7.4 \mu\text{g l}^{-1}$ yielded an uptake length 55% longer than that measured by ^{33}P at the ambient concentration ($2.9 \mu\text{g l}^{-1}$). Estimates made using this approach, therefore, provide only an upper bound for uptake length.

A number of mass balance studies have shown phosphorus removal from solution downstream from municipal and agricultural sources of phosphorus (Keup 1968; Taylor & Kunishi 1971; Johnson *et al* 1976; Harms *et al* 1978; Hill 1982).

In these studies, DIP concentrations declined longitudinally from peaks sometimes exceeding $1000 \mu\text{g l}^{-1}$ (Harms *et al* 1978), with net uptake rates in the range of 10 to $>100 \text{ mg m}^{-2} \text{ day}^{-2}$ (in most cases, these uptake rates are inferred because few studies reported net uptake directly). Phosphorus apparently accumulates in the sediments by physical adsorption (as discussed below) during periods of steady flow, and is then transported downstream as particulate load during storms (Cahill *et al* 1974; Harms *et al* 1978; Verhoff & Melfi 1978; Verhoff *et al* 1979).

As phosphorus leaves the dissolved form in the water column, it may be transferred either to the sediments or to suspended solids (seston) within the water column. Uptake by seston may be negligible in very small streams (e.g. 1.3% of total uptake; Newbold *et al* 1983a), but increases in importance with stream size (Ball & Hooper 1963; Paul *et al* 1989) and may account for nearly all of the uptake in large rivers with true phytoplankton populations (Décamps *et al* 1984). As in marine and lacustrine environments, most of the sestonic uptake appears to occur within the smallest size fractions (e.g. $<1 \mu\text{m}$; Corning *et al* 1989). Phosphorus transferred to seston may subsequently settle to the sediments. Simmons and Cheng (1985) concluded that this was the major pathway for removal of phosphorus from the water column in a river receiving sewage effluent.

Biological uptake

Phosphorus is removed from the water by algae (including cyanophyte bacteria), heterotrophic microbes, macrophytes, bryophytes and riparian plants. The kinetics of phosphorus uptake by planktonic algae have received extensive attention [see Cembella *et al* 1984a, 1984b], and the fundamentals undoubtedly apply to attached algae. Uptake generally follows Michaelis–Menten kinetics (see equation (10)). Bothwell (1985) found that K_s for periphytic river diatoms ranged from 0.5 to $7.2 \mu\text{g l}^{-1}$, or below that for most phytoplankton populations. Algae (and bacteria) can take up phosphorus at a much greater rate than they can utilize it for growth so that V_{max} can vary greatly, declining as cells accumulate phosphorus (Rhee 1974). As a result, steady-

state growth is saturated by concentrations very much lower than K_s (Droop 1973; Rhee 1974). Uptake of phosphorus by attached algae is also influenced by transport of phosphorus to and into the algal biofilms (section 7.3).

Few data exist to evaluate the relative importance of ecosystem components in taking up phosphorus from the water column. In Walker Branch, which is well shaded, 60% of the phosphorus uptake in the summer was accounted for by large detritus ($>1 \text{ mm}$), 35% by fine particles ($<1 \text{ mm}$) and 5% by the epilithon, consisting primarily of diatoms (Newbold *et al* 1983a). The phosphorus content of leaf detritus increases during decomposition (Kaushik & Hynes 1968; Meyer 1980), and the rate of phosphorus uptake correlates with measures of metabolic activity (Gregory 1978; Mulholland *et al* 1984; Elwood *et al* 1988). In less shaded streams and rivers, the epilithon and associated algae are probably the dominant fate of phosphorus (Ball & Hooper 1963; Peterson *et al* 1985). Ball and Hooper (1963) did not make a mass accounting for the phosphorus taken up, but they did find that weight-specific uptake by macrophytes (*Chara*, *Fontinalis* and *Potamogeton*) was far slower than by periphyton.

Adsorption

Adsorption and desorption of phosphorus on to organic and inorganic surfaces are continual kinetic processes. Thus, some portion of the phosphorus cycle (e.g. as observed via ^{32}P injection) involves entirely abiotic processes. Unfortunately, few studies have addressed phosphorus adsorption from a kinetic standpoint (except see Pomeroy *et al* 1965; Li *et al* 1972; Furumai *et al* 1989), so that it is difficult to evaluate the magnitude of this cycling. Studies of ^{32}P uptake by epilithon and by particulate organic matter have found that uptake is small or negligible under sterile conditions (Gregory 1978; Elwood *et al* 1981a; Paul *et al* 1989). These studies, however, involved very low phosphorus concentrations and did not include large quantities of inorganic fine particles.

Most studies of phosphorus adsorption in rivers have focused not on the kinetic exchange of phosphorus, but on the role of sediments in controlling

or 'buffering' dissolved phosphorus concentrations. Adsorption of phosphorus on to natural river sediments and suspensoids generally corresponds to a Langmuir isotherm (Green *et al* 1978; McCallister & Logan 1978; Stabel & Geiger 1985; Furumai *et al* 1989), which has the form:

$$X = bkC/(1 + kC) \quad (12)$$

in which X is the quantity of adsorbed phosphorus per mass of sediment, C is the dissolved phosphorus concentration, b is the 'adsorption maximum' in units of X , and k is the 'adsorption energy' in units of $1/C$. At phosphorus concentrations below 0.1–1.0 mg l⁻¹, the isotherms are approximately linear (i.e. $kC \ll 1$). For fine particles (<0.1 mm), which account for nearly all of the sorption capacity (Meyer 1979), the slope (bk) of the isotherms ranges from about 0.1 to 1.0 µg P g⁻¹ sediment per µg P l⁻¹ water.

Sediment particles are often characterized in terms of their 'equilibrium phosphorus concentration' (EPC), which is the water concentration at which phosphorus is neither adsorbed nor desorbed (White & Beckett 1964; Klotz 1988). The EPC reflects the quantity, X , of adsorbed phosphorus and, in terms of the Langmuir isotherm, represents the value of C that satisfies equation (12). Sediments that enter rivers may either desorb phosphorus to the water (Mayer & Gloss 1980; Gloss *et al* 1981; Grobbelaar 1983; Viner 1988), or adsorb phosphorus from the water (Kunishi *et al* 1972) depending on whether the initial EPC exceeds the water phosphorus concentration. The EPC of stream sediments is often near the stream water phosphorus concentration (Taylor & Kunishi 1971; Meyer 1979; Mayer & Gloss 1980; Hill 1982; Klotz 1985, 1988; Munn & Meyer 1990), indicating rapid equilibration. This equilibration has frequently been interpreted as evidence that the sediments control or 'buffer' stream water concentrations. Such buffering, however, implies a net uptake or release of phosphorus by the sediments which, under steady conditions, will diminish as the sediment EPC adjusts to the concentration of the source water. Thus, it would seem premature to conclude that the sediment EPC controls the stream water concentration (rather than the converse) without additional information about source water con-

centrations, the actual quantity of sediments in the streambed, or both.

In general, we would expect sediments to influence phosphorus concentrations when: (1) there is an abundance of fine inorganic particles (e.g. several hundred kg m⁻²); and (2) a large discrepancy exists between the EPC of sediments entering the river and the concentration of phosphorus entering the river. These conditions would explain the prolonged periods of high net phosphorus removal downstream from pollution sources discussed above. In streams and rivers with few fine inorganic sediments and low dissolved phosphorus inputs, however, the role of adsorption in controlling phosphorus concentrations may be minimal, and perhaps exceeded by the influence of biological processes. Mulholland *et al* (1990), for example, observed an apparent transition from biotically dominated uptake to sorption-dominated uptake at about 5 µg l⁻¹, a concentration that might have saturated biological uptake capacity.

Regeneration

Where field injections of ³²P have been made, the loss of ³²P from the water has not been accompanied by commensurate depletion of stable phosphorus (Ball & Hooper 1963; Newbold *et al* 1983a; Mulholland *et al* 1985b), implying that regeneration of phosphorus approximately balances gross uptake. Other evidence for regeneration comes from direct observation of ³²P in stream water for several weeks following a ³²P release (Elwood & Nelson 1972), and from ³²P accumulation in detritus and periphyton placed into a stream after the initial labelling (Ball & Hooper 1963; Elwood & Nelson 1972). Similar results have been obtained in laboratory streams (Short & Maslin 1977; Paul & Duthie 1989). Studies with ³²P have shown that phosphorus associated with epilithon and detritus returns to the water with a turnover time of a week or less, whereas turnover in fine sediments may be an order of magnitude slower (Ball & Hooper 1963; Elwood & Nelson 1972; Newbold *et al* 1983a).

Regeneration of phosphorus from the biota may occur via: (1) excretion of phosphorus (either as DIP or DOP) from living algae and bacteria;

(2) release of phosphorus upon death and lysis of cells; and (3) ingestion followed by egestion, excretion, and death of animal consumers. Although the first two pathways may in some cases be significant (Barsdate *et al* 1974; Lean & Nalewajko 1976; DePinto 1979), there is a growing consensus from marine and lacustrine studies that animal consumers, particularly Protozoa and other microscopic animals, represent the major pathway. Regeneration by consumers is discussed in section 7.8.

A portion of the phosphorus lost from organisms may be in the form of dissolved organic phosphorus (DOP). Much of the DOP released may be hydrolysed rapidly to DIP by alkaline phosphatase and ultraviolet degradation (Francko 1986). Alkaline phosphatase, which is capable of hydrolysing a range of organic phosphorus compounds, has been detected in the sediments of some streams (Sayler *et al* 1979; Klotz 1985). However, the bulk of the DOP that is found in natural waters is not hydrolysed by alkaline phosphatase (Herbes *et al* 1975; Jordan & Dinsmore 1985; Hino 1989). Mulholland *et al* (1988) found that about 12% of ^{32}P released from decomposing leaf detritus was organic with molecular size >5000 daltons. This organic fraction appeared to be far less available for utilization than PO_4 , with only about 10% utilized within 24 hours of incubation. High molecular weight organic phosphorus has been identified in other river and lake waters (Lean 1973; Downes & Paerl 1978; Peters 1978, 1981; White *et al* 1981) where it has similarly been shown to be biologically available, but at a slower rate than PO_4 (Pearl & Downes 1978; Peters 1981). It remains unclear whether utilization of DOP can occur directly (Smith *et al* 1985), possibly involving enzymatic activity on cell surfaces (Ammerman & Azam 1985), or whether the DOP is first hydrolysed within the water. Whatever the ecological significance of this distinction, it is clearly important to the interpretation of ^{32}P kinetics. The potential role of DOP in cycling has special significance for rivers because DOP is highly transportable yet unavailable for rapid uptake and thus could contribute substantially to spiralling length.

Phosphorus spiralling in a woodland stream

An extensive quantification of phosphorus spiralling has been attempted for only one stream, Walker Branch, Tennessee (Newbold *et al* 1983a). This description was obtained by fitting a multi-compartmental model to the ^{32}P data to estimate transfer coefficients among all compartments (Fig. 7.7). From the model, spiralling within each compartment is described with three parameters: the residence time in the compartment, the fraction of the cycling phosphorus flux passing through the compartment, and the downstream velocity of the compartment (Table 7.1). The spiralling length was 190 m, consisting of 165 m of travel in the water (as described above), and 25 m of travel in the particulate compartments (CPOM, FPOM and epilithon). Phosphorus taken up by consumers had a downstream travel distance of 2 m, but since only 2.8% of the flux passed through this compartment, the contribution to total spiralling length was only 0.06 m. Although dissolved phosphorus accounted for most of the spiralling length, its turnover time of 75 min was a small fraction of the 18 days required to complete a cycle.

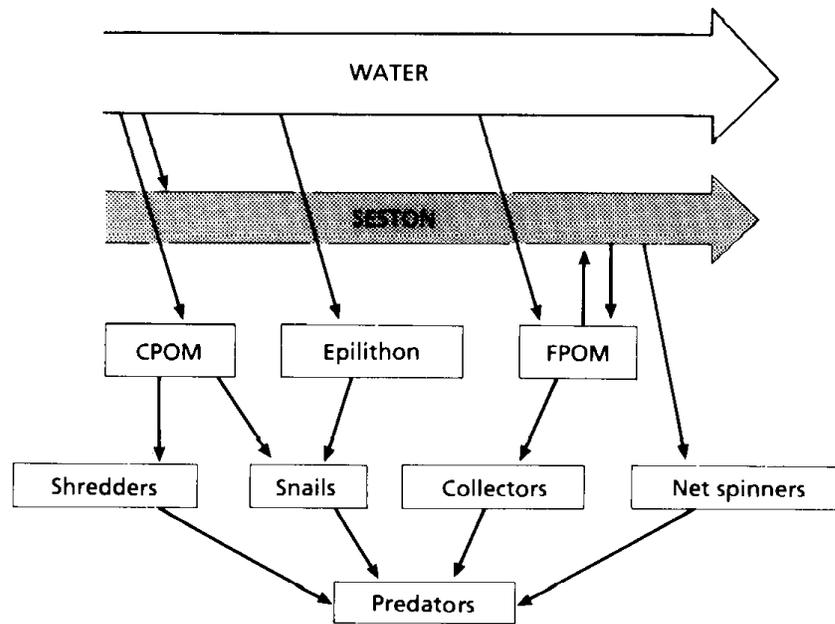
Walker Branch is highly retentive of phosphorus. In effect, the biotic phase 'slows' the average movement of phosphorus downstream by a factor of about 300 relative to the water velocity. Stated another way, the standing stock of phosphorus is 300 times greater than in the absence of retention. The snail *Elimia* (= *Goniobasis*) *claeiformis* plays a large role in this retention, accounting for 23% of the standing stock exchangeable phosphorus, and drifting downstream at a velocity of $<1 \text{ cm day}^{-1}$.

7.7 NITROGEN

Nitrogen cycle

Nitrogen is a fundamental constituent of protein and, like phosphorus, its availability can frequently limit algal and microbial productivity. The major pathways of the nitrogen cycle in aquatic systems are shown in Fig. 7.8 (see also Kaushik *et al* 1981; Sprent 1987), although not all of these pathways have been studied extensively

Fig. 7.7 Ecosystem compartments and flows used to analyse spiralling of phosphorus in a small woodland stream (from Newbold *et al* 1983a). In addition to the phosphorus fluxes indicated by arrows on the diagram, every compartment releases phosphorus directly back to the water compartment. These arrows are omitted for simplicity. Dynamics of the water and seston compartments were described by partial differential equations similar to equation (9) and coupled to other compartments as illustrated in Fig. 7.3.



in rivers. The nitrogen cycle in rivers is more complex than the phosphorus cycle in several important respects. First, the processes of nitrogen fixation and denitrification involve exchanges

with atmosphere, so that cycling of nitrogen cannot be considered closed with respect to the air-water interface. (Atmospheric exchanges of ammonia may also be significant under some

Table 7.1 Calculation of spiralling indices for phosphorus in Walker Branch (from Newbold *et al* 1983a)

Compartment	t_i (days)	v_i (m day ⁻¹)	s_i (m)	b_i	S_i (m)
Water	0.052	3200	165	1.0	165
Particulates					
CPOM [†]	6.9	0.06	0.40	0.60	0.24
FPOM (fast) [‡]	6.9	7.4	51	0.27	13
FPOM (slow) [‡]	99.0	1.4	141	0.080	11
Epilithon	5.6	0.0	0.0	0.054	0.0
Total particulates	14.0*	1.8*	25*	1.0	25
Consumers					
Snails	150	0.005	0.77	0.024	0.019
Shredders	76	0.13	9.8	0.0002	0.0030
Collectors	105	0.12	13	0.003	0.03
Net spinners	220	0.0	0.0	0.007	0.0
Predators	14	0.007	0.10	0.008	0.0008
Total consumers	150*	0.013	2.0*	0.028	0.056
Total	18*	10	190	1.0	190

* Weighted average; [†] coarse particulate organic matter (>1 mm); [‡] fine particulate organic matter (<1 mm). Two turnover rates, 'fast' and 'slow', were resolved from the ³²P dynamics of the FPOM compartment. t_i is average residence time in compartment i ; v_i is average downstream velocity of compartment i . Average travel distance in a compartment, $s_i = v_i t_i$. The contribution of compartment i to spiralling length is $S_i = b_i s_i$, where b_i is the probability of passing through compartment i . Particulate and consumer turnover lengths are the sums of S_i values within these categories.

circumstances.) Second, in addition to its role as a fundamental cellular constituent in all organisms, nitrogen is also involved in biologically mediated redox reactions, such as nitrification which yields energy for metabolism and consumes oxygen, and denitrification, in which nitrate serves as a terminal electron acceptor. These processes involve specialized organisms and occur with very different stoichiometric coupling to carbon flow than does cellular assimilation of nitrogen. Finally, there are two major sources of inorganic nitrogen for algal and microbial assimilation (NH_4 and NO_3), rather than one (PO_4) in the phosphorus cycle. Understanding of the nitrogen cycle in rivers is limited not only by the complexity of the cycle, but by the fact that very few isotopic tracer studies have been conducted in rivers or in river-simulating microcosms. The available isotope,

^{15}N , is not radioactive, but is otherwise more difficult and expensive to work with than are the radioisotopes of phosphorus.

Estimates by Meybeck (1982) of worldwide average concentrations of dissolved nitrogen in unpolluted rivers are ($\mu\text{g l}^{-1}$): dissolved organic nitrogen (DON) 260; nitrate 100; ammonium 15; nitrite 1. In agricultural watersheds in North America, DON averages about $1000 \mu\text{g l}^{-1}$, and dissolved inorganic nitrogen typically ranges from ~ 700 to $5000 \mu\text{g l}^{-1}$ (Omernik 1977). Algae and other micro-organisms tend to use ammonium in preference to nitrate, which must be reduced before it can be assimilated (Sprenst 1987). Based on results from lacustrine and marine ecosystems (Eppley *et al* 1979; Axler *et al* 1982) it is reasonable to conjecture that in many streams and rivers, ammonium supplies a substantial part, if not the

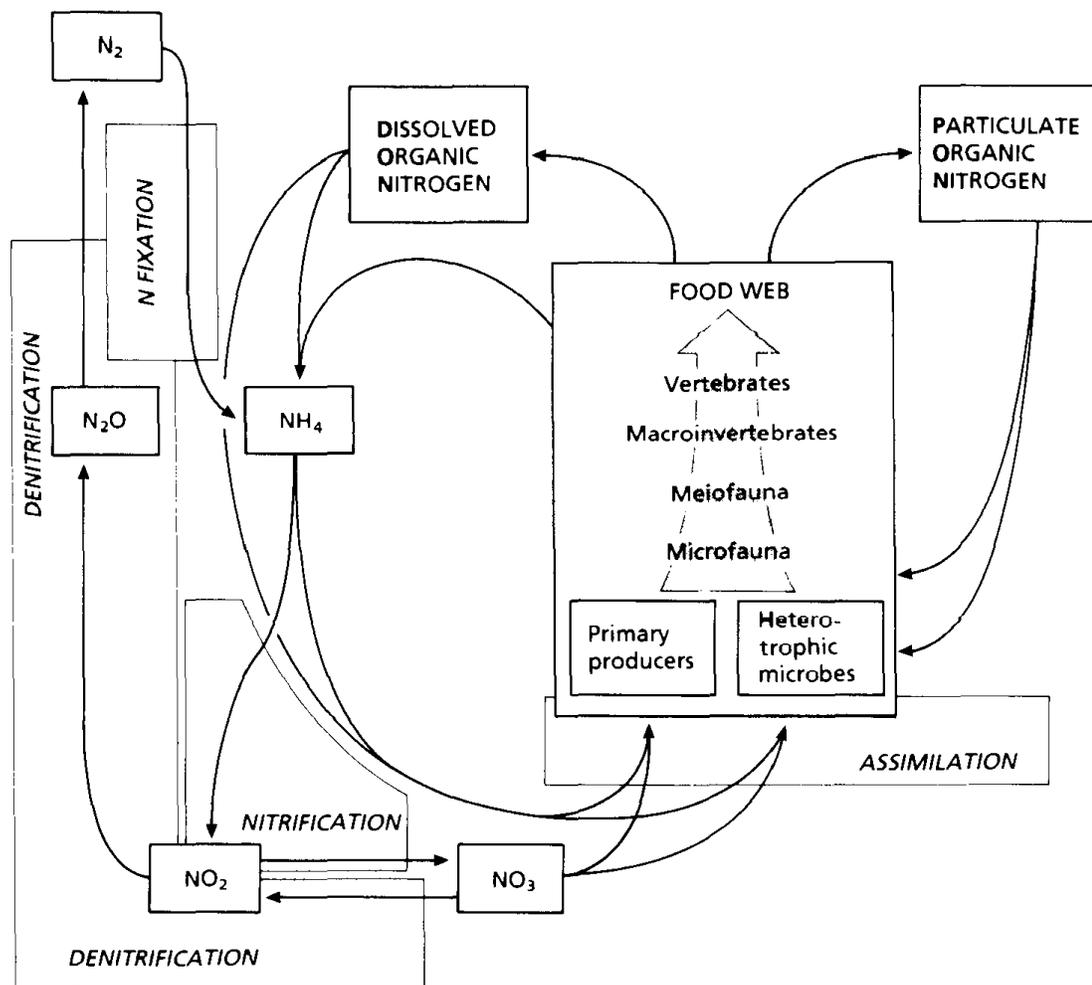


Fig. 7.8 Schematic of the nitrogen cycle in streams and rivers.

majority, of the nitrogen assimilation by algae and heterotrophic micro-organisms. Much of this ammonium may be supplied by excretion from consumers and cycle rapidly (and over short distances) back into the microbial community. Stanley and Hobbie (1981), using ^{15}N , found that uptake by river plankton of ammonium exceeded that of nitrate by a factor of three, while the ammonium concentration averaged only about half that of nitrate. Thus, the ammonium pool turned over approximately six times faster than the nitrate pool. The uptake of dissolved inorganic nitrogen (DIN, consisting of nitrate plus ammonia) averaged about $5 \text{ mg m}^{-2} \text{ h}^{-1}$, but peaked at near $70 \text{ mg m}^{-2} \text{ h}^{-1}$ in the summer at maximum photoplankton concentrations. On an annual basis, the utilization of DIN within the 60-km study reach exceeded upstream inputs to the reach by a factor of three, corresponding to an uptake length of 20 km, with an average turnover time of the DIN pool of about 10 days. In the summer, under high demand and low flows, turnover times fell to 3–10 h, corresponding to uptake lengths of <1 km. Stanley and Hobbie also concluded that bacteria may have played an important role, in addition to phytoplankton, in taking up the DIN, and that approximately one-third of the DON entering the reach was converted to DIN, presumably through microbial assimilation and regeneration.

Biological uptake

Little is known about the magnitude of ammonium utilization by benthic organisms. Several studies have documented rapid uptake by the benthos of ammonium introduced at enriching levels (McColl 1974; Newbold *et al* 1983b; Richey *et al* 1985; Hill & Warwick 1987). Ammonium, however, is similar to phosphorus in that it is strongly subject to physical sorption and cells can incorporate ammonia temporally in excess of growth requirements (Eppley & Renger 1974; Conway & Harrison 1977). Thus it is difficult to draw inferences from these studies about the utilization of ammonium under natural concentrations.

As with ammonium there are no studies other than that of Stanley and Hobbie (1981) of nitrate

gross uptake under undisturbed conditions. However, there have been a number of mass balance studies observing disappearance of nitrate, which has in some cases been equated to a net incorporation of nitrate by benthic algae and heterotrophic micro-organisms. Fisher *et al* (1982) and Grimm (1987) observed longitudinal declines in nitrate concentrations in a desert stream associated with rapid growth of benthic algae following scouring storms. Maximum calculated uptake rates were $240 \text{ mg m}^{-2} \text{ day}^{-1}$. Fisher *et al* (1982) noted that comparing net primary production to calculated uptake rates gave a C:N ratio of 4:1, or lower than the Redfield ratio of 6.6:1 (Redfield *et al* 1963), suggesting that some of the net nitrate uptake went to other fates, such as denitrification.

Uptake of experimentally injected nitrate has been observed in several streams (McColl 1974; Sebetich *et al* 1984; Triska *et al* 1989a; Aumen *et al* 1990; Munn & Meyer 1990; Webster *et al* 1991) in which background DIN concentrations were $< 150 \mu\text{g l}^{-1}$. In other streams, all with background concentrations $> 100 \mu\text{g l}^{-1}$, no net uptake was observed (McColl 1974; Richey *et al* 1985; Aumen *et al* 1990). The relation to DIN, however, is not entirely consistent, and background ammonium concentrations (not always reported) may be an important factor. In the most detailed study, where substantial net uptake of added nitrate occurred over 9 days of injection (Triska *et al* 1989a, 1989b), background ammonium concentrations were undetectable, while background nitrate was $25\text{--}50 \mu\text{g l}^{-1}$.

Kim *et al* (1990) analysed uptake kinetics of nitrate added to artificial channels in which periphyton grew on Plexiglas slides. They obtained half saturation constants for uptake (K_s) in the range of $50\text{--}80 \mu\text{g l}^{-1}$ from laboratory batch experiments, and then fitted an uptake model (section 7.4) to the dynamics of nitrate injected into their channels. From this, they obtained values for maximum uptake in the range of $0.15\text{--}0.65 \mu\text{g N s}^{-1} \text{ g}^{-1}$ ash-free-dry-mass (AFDM) of periphyton.

Nitrification

Nitrification, the biological oxidation of ammonium to nitrite and then to nitrate, seems to

occur in streams and rivers whenever both ammonium and oxygen are available. It is of particular interest as a water quality issue because it can reduce potentially toxic levels of ammonium discharges. Nitrification, however, consumes dissolved oxygen, and so exacerbates the oxygen depletion associated with oxidation of organic wastes. Much of the dissolved and particulate organic nitrogen in waste discharges may also ultimately be nitrified, after degradation to ammonium. Rates of nitrification in rivers, therefore, are sometimes reported as the rate at which both ammonium and organic nitrogen are converted to nitrate. These rates vary approximately in the range of 0.1–0.5 day⁻¹ depending on temperature, the proportion of the nitrogen source that is ammonium, and other factors (McCutcheon 1987). Nitrification may play a large role in maintaining ammonium levels in unpolluted streams at low levels. Triska *et al* (1990) found that nitrification occurred in the sediments, reducing relatively high ammonium levels in influent groundwater to low levels observed in the stream. Nitrification appears to be associated largely with the sediments in streams and smaller rivers (Matulewich & Finstein 1978; Cooper 1983; Cooper 1984) but may occur largely in suspension in larger rivers (McCutcheon 1987). Estimated benthic rates of nitrification in streams range from 29 mg m⁻² day⁻¹ (Chatarpaul *et al* 1980) to 2.5 g m⁻² day⁻¹ (Cooper 1984).

Denitrification

Denitrification, the reduction of nitrate to dinitrogen, is carried out by bacteria using the nitrate as the terminal electron acceptor for oxidative metabolism in the absence of oxygen. Denitrification is included in the general category of dissimilatory nitrate reduction, which can also include reduction of nitrate to ammonium. Denitrification can be a significant pathway for loss of nitrogen from the river and has been implicated in explaining downstream declines in nitrogen concentrations in several watersheds (Kaushik *et al* 1975; Hill 1979, 1988; Swank & Caskey 1982; Cooper & Cooke 1984). Most estimates of denitrification in streams fall into the range of 10–200 mg m⁻² day⁻¹ (Chatarpaul &

Robinson 1979; Cooper & Cooke 1984; Duff *et al* 1984b; Hill & Sanmugadas 1985; Christensen & Sørensen 1988; Seitzinger 1988; Christensen *et al* 1989). Nearly all of these measurements, however, have been conducted in streams with relatively high nitrate concentrations (i.e. 0.5–10 mg l⁻¹), and in streams that are not nitrate enriched normal rates of denitrification may be much lower (Duff *et al* 1984b; S.P. Seitzinger, personal communication).

Although denitrification requires anoxic conditions, it has been observed in aerated sediments and in relatively thin epilithic films (Nakajima 1979; Duff *et al* 1984b; Duff & Triska 1990). Evidently, denitrification occurs in microzones of anoxia within the sediments and biofilms. Oxygen produced by benthic algae may inhibit denitrification (Duff *et al* 1984b) resulting in diel variations in denitrification rates (Christensen *et al* 1990).

Denitrification requires an organic carbon source and proceeds faster where more carbon is available in the water and in the sediments (Hill & Sanmugadas 1985; Duff & Triska 1990). Typical denitrification rates of 10–200 mg m⁻² day⁻¹ are equivalent to the respiration of 0.03–0.7 g O₂ m⁻² day⁻¹. By comparison, oxygen consumption in rivers generally ranges from 0.2 to 10 g O₂ m⁻² day⁻¹ (Bott *et al* 1985). Thus, denitrification may contribute a significant portion of the oxidative metabolism in streams where nitrate supply is high and appropriate habitat and carbon resources are available. Denitrification may occur simultaneously with nitrification (Duff *et al* 1984a; Cooke & White 1987). In Little Lost Man Creek, California, USA, nitrogen enters the deep sediments (hyporheos) as ammonium, mixes with oxygenated interstitial water and nitrifies (Triska *et al* 1990), yielding a net downstream increase in nitrogen concentrations. Yet significant denitrification also occurs within the hyporheos, presumably in anoxic microzones (Duff & Triska 1990). Chatarpaul *et al* (1980) found that tubificid worms in sediments enhanced both nitrification and denitrification.

Most of the measurements reported above estimated denitrification by the acetylene block method (Balderston *et al* 1976; Yoshinari *et al* 1976), although ¹⁵N (e.g. van Kessel 1977;

Chatarpaul & Robinson 1979) and direct measurement of nitrogen evolution (Seitzinger 1988) have also been employed. The acetylene block method is subject to various uncertainties, the most serious of which is that it interferes with nitrification. As a result, the method can greatly underestimate denitrification when it is coupled to nitrification of an ammonia source (SP Seitzinger, CP Nielson, J Caffrey & PB Christenson, unpublished data).

Nitrogen fixation

Blue-green algae and micro-organisms fix nitrogen in streams and rivers, but few measurements have been made. Horne and Carmiggelt (1975) reported nitrogen fixation by the blue-green alga *Nostoc* of 42–360 mg N m⁻² year⁻¹, while Francis *et al* (1985) estimated nitrogen fixation in pool sediments of 5.1 g N m⁻² year⁻¹. Even these higher values, however, are small in comparison with other nitrogen fluxes as noted above.

7.8 THE ROLE OF CONSUMERS

Animals in the food web may account for a considerable portion of the nutrient cycle, but their influence on nutrient cycling involves, in addition: (1) direct influences on prey populations, which may 'cascade' through several trophic levels; (2) indirect influences of regenerated nutrients; and (3) indirect influences of physical transformations and translocations of nutrients and of the physical habitat (Kitchell *et al* 1979).

Algal grazers have been reported to assimilate 30–98% of algal nitrogen uptake (Grimm 1988) and roughly 80% of algal phosphorus uptake (Mulholland *et al* 1983). This is consistent with many studies showing that grazing macroinvertebrates and fish maintain biomass of epilithic algae substantially below levels that would occur in the absence of grazers (e.g. McAuliffe 1984; Jacoby 1985; Stewart 1987; Power *et al* 1988; Feminella *et al* 1989; Hart & Robinson 1990). Indirect, or cascading, control of algal biomass by predators of grazers has also been demonstrated (Power *et al* 1985; Gilliam *et al* 1989; Power 1990). The weight-specific productivity of grazed algae normally exceeds that of ungrazed algae

(Kehde & Wilhm 1972; Summer & McIntire 1982; Gregory 1983; Lamberti & Resh 1983; Lamberti *et al* 1987, 1989; Hill & Harvey 1990), and a similar effect has been observed on phosphorus turnover rate (Mulholland *et al* 1983). However, the net effect of depressing biomass and increasing biomass turnover is normally to decrease productivity (and nutrient uptake) on an areal basis, and only slight, or statistically non-significant, cases of an actual stimulation of areal productivity have been observed.

The possibility that some moderate level of grazing might stimulate, or maximize, areal productivity is of interest because the phenomenon has been observed in lentic systems and microcosms (Cooper 1973; Flint & Goldman 1975; Bergquist & Carpenter 1986; Elser & Goldman 1991), and is usually attributed to the effect of consumers in regenerating nutrients, as predicted by nutrient cycling models (Lane & Levins 1977; Carpenter & Kitchell 1984). Stimulation may have gone undetected in streams because experiments have employed flumes that are too short to observe recycling effects (i.e. much shorter than the spiralling length). However, analysis of a spiralling model (Newbold *et al* 1982b) indicated that the stimulation effect (which would produce a shorter spiralling length) is possible in streams, but unlikely to occur because: (1) streams do not suffer depletion of the limiting nutrient in the same manner as lakes or closed systems (section 7.3); and (2) a simultaneous effect of grazers, which is to dislodge and suspend particles, tends to nullify the benefits of regeneration.

In woodland streams, heterotrophic microbes may take up far more inorganic nutrients from the water than do autotrophs (e.g. Table 7.1). It appears, however, that relatively little of this uptake is assimilated or regenerated by macroinvertebrate consumers. In Walker Branch, Tennessee, for example, where detritus accounts for 95% of the phosphorus uptake, <3% of this is eventually assimilated by macroinvertebrates (Table 7.1). Studies of detritus processing have similarly shown that carbon assimilation by macroinvertebrates is only a small percentage of carbon lost to microbial respiration (Cummins *et al* 1973; Fisher & Likens 1973; Webster 1983; Smock & Roeding 1986; Petersen *et al* 1989). In

marine and lacustrine environments, the protozoans and other very small animals (i.e. the meiofauna) assimilate much of the microbial production and play a major role in nutrient regeneration (e.g. Johannes 1965; Andersen *et al* 1986; Caron & Goldman 1990). Work in riverine environments, although still limited, suggests an equally strong role for meiofauna (Findlay *et al* 1986; Bott & Kaplan 1990; Crosby *et al* 1990). In streams and rivers, the meiofauna may include early-instar insect larvae, as well as protozoans and animals that remain microscopic throughout their life history. Whether energy and nutrients from the meiofauna can then pass to higher trophic levels via predation remain essentially uninvestigated.

Macroinvertebrate consumers exert a substantially larger effect on nutrient cycling than their energy consumption would suggest. Macroinvertebrate shredders increase significantly the speed the conversion of large detrital particles to small particles (e.g. Petersen & Cummins 1974; Wallace *et al* 1982; Cuffney *et al* 1990) with consequent effects on particle transport. Cuffney *et al* (1990) found that removal of macroinvertebrate populations from a small stream reduced annual transport of seston by 40%. Webster (1983) estimated that macroinvertebrate activity accounted for 27% of annual seston transport, and as much as 83% of transport during low summer flow. From the standpoint of phosphorus and nitrogen transport, these effects are probably not important since, as we have seen, turnover lengths in headwater streams are short. The transport does, however, increase the organic carbon turnover length, depleting carbon stocks in headwater reaches, and so depresses the available substrate for energy and nutrient utilization.

Newbold *et al* (1982b) hypothesized that, by increasing the ratio of surface to volume of detrital particles, leaf shredders might enhance microbial activity and nutrient uptake. Experimental tests, however, showed little evidence of this effect. Shredders instead decrease phosphorus utilization both through direct assimilation of the detrital pool and through increasing downstream particulate losses (Mulholland *et al* 1985a).

Net-spinning caddisfly (Trichoptera) and blackfly (Diptera: Simuliidae) larvae filter particles

from the water column and therefore actually reduce transport. Although downstream declines in seston transport have been observed below reservoirs and lake outfalls where filter feeders are abundant (e.g. Maciolek & Tunzi 1968) and Ladle *et al* (1972) inferred a substantial effect of *Simulium* on particle transport in a chalk stream, it appears that filter feeders in most streams and rivers exert a small or insignificant effect on total particle transport (e.g. McCullough *et al* 1979; Newbold *et al* 1983a). However, they may substantially reduce the transport of particles in specific high-quality food classes (Georgian & Thorp 1992).

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