

CHAPTER 5

Nutrient Spiraling and Transport in Streams: The Importance of In-Stream Biological Processes to Nutrient Dynamics in Streams

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INTRODUCTION

Hynes (1970) observed that living organisms in streams may significantly affect nutrient concentrations, but our understanding of these effects remains elusive and subject to debate (Cardinale, 2011a,b; Baulch et al., 2011). The possible role of biotic, in-stream processes for affecting nutrients is important to understanding how upstream processes are linked to downstream responses (Vannote et al., 1980; Mulholland et al., 1995), to the biogeochemical interpretation of watershed exports (eg, Bernhardt et al., 2005), and to delivery of nutrients to coastal waters (Doney, 2010).

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Some of the first evidence that biota alter nutrient concentrations came from observations of longitudinal declines (eg, Neel, 1951; Minckley, 1963; Hill, 1979) and temporal variations (eg, Minckley, 1963; Edwards, 1974) that could be linked to biological activity in streams (see Hynes, 1970 for citations to additional early literature). However, as reviewed by Mulholland and Webster (2010), such evidence was slow to accumulate and for several decades, in-stream processes were seen as having little influence on stream chemistry. If such influences are indeed small, then stream chemistry directly reflects the outputs of the upslope terrestrial ecosystem—outputs that are otherwise difficult to measure. This is the basis for the small watershed concept of Bormann and Likens (1967), which has yielded many insights into the hydrology and biogeochemistry of terrestrial ecosystems (eg, Johnson et al., 1969; Vitousek and Reiners, 1975; Bormann and Likens, 1979; Aber et al., 1989; Murdoch and Stoddard, 1992). Although Bormann and Likens (1967) noted the potential importance of in-stream processes, the possible implications for watershed biogeochemical inferences have only recently received serious consideration (eg, Bernhardt et al., 2005; Brookshire et al., 2009; Mulholland and Webster, 2010).

It is possible that Hynes (1970) inferred the importance of biota in part from early evidence that stream biota rapidly assimilate nutrients from the stream's water column. Several studies reported biological uptake of radionuclides in streams (Davis and Foster, 1958; Whitford and Schumacher, 1961, 1964; Kevern, 1964; Garder and Skulberg, 1966; Cushing, 1967; Cushing and Rose, 1970), and uptake of nitrogen by decaying leaves was documented by Kaushik and Hynes (1968) and Mathews and Kowalczewski (1969). None of these studies, however, measured the magnitude of nutrient removal from the water column. The earliest such quantification came from a release of ^{32}P -labeled phosphate to the Sturgeon River, Michigan, by Ball and Hooper (1963), who found that phosphate traveled, on average, 1400 m downstream, remaining in the water column for less than an hour before being taken up on the streambed, primarily by benthic periphyton and macrophytes. Subsequent studies with ^{32}P in Walker Branch, Tennessee, confirmed the rapid uptake of phosphorus and showed that the average travel distance, or uptake length, could be used to estimate the areal uptake of phosphorus onto the streambed (Nelson et al., 1969; Elwood and Nelson, 1972; Newbold et al., 1981). Uptake length measurements were extended to nitrogen through the use of ^{15}N -labeled ammonium (eg, Peterson et al., 2001) and nitrate (eg, Mulholland et al., 2008). Uptake lengths of both phosphorus and nitrogen have also been estimated using

short-term nutrient enrichments, as opposed to tracer additions ([Stream Solute Workshop, 1990](#)). Although the latter approach overestimates the ambient uptake length and underestimates areal uptake ([Mulholland et al., 1990, 2002; Payn et al., 2005](#)), it has nonetheless, added a large body of evidence confirming the active uptake of nutrients in streams ([Ensign and Doyle, 2006; Mulholland and Webster, 2010](#)).

Rapid nutrient uptake suggested the potential for biota to affect stream nutrient concentrations (eg, [Keup, 1968](#)), but it was apparent even from the earliest studies that rapid uptake could occur with little effect on nutrient concentration. Although 90% of the ^{32}P that [Ball and Hooper \(1963\)](#) added to the Sturgeon River was taken up within their 4800-m study reach, concentrations of natural soluble reactive phosphorus remained effectively uniform throughout the reach. [Ball and Hooper \(1963\)](#) concluded that the uptake was replaced by mineralization of phosphorus from the stream-bed and that “there was rapid cycling of phosphorus atoms as they moved downstream.” However, the downstream movement complicated their attempts to quantify the cycling. They noted, for example, that the level of recycling of ^{32}P (the re-uptake of ^{32}P released from the streambed) was “much lower” than observed in lakes ([Hayes et al., 1952; Rigler, 1956](#)) or microcosms ([Whittaker, 1961](#)) because the ^{32}P “is continuously removed by the current.” At the time, nutrient cycling was viewed from the perspective of a bounded ecosystem within which a nutrient atom might cycle many times before “export” ([Likens and Bormann, 1974](#)). From this perspective, nutrient cycling in streams appeared minimal ([Scott, 1958](#)). Transport was the dominant process. [Webster and Patten \(1979\)](#) proposed an alternate perspective for streams: cycling depends on the scale over which it is observed. While cycling at a single point in a stream may indeed be negligible, cycling does occur on the scale of a reach. That is, each cycle involves a downstream displacement, so that cycling in streams might better be termed spiraling ([Webster and Patten, 1979](#)). The downstream distance required for one complete cycle, which [Newbold et al. \(1981\)](#) termed the spiraling length, expresses the characteristic scale of cycling in the stream. [Newbold et al. \(1981, 1983\)](#) formalized spiraling length as consisting of an uptake length plus a turnover length, which is the additional downstream distance traveled, on average, prior to mineralization. The latter, organic portion of the spiral transports nutrient in unavailable form, thus reducing the concentration of available inorganic nutrient. Within a whole river network, the typical phosphorus or nitrogen atom cycles several tens of times ([Ensign and Doyle, 2006](#)). There may be no longitudinal

concentration gradient even though nutrients are being rapidly used and reused (Brookshire et al., 2009).

The spiraling concept would appear to explain, or at least be consistent with, the absence of strong biotic effects on stream nutrient concentrations: what is taken up by the biota is simply replaced by mineralization. This view may have slowed recognition that biota actually do affect concentrations. However, the spiral actually involves temporal delay and downstream transport between uptake and mineralization, and it is through these processes that nutrient concentrations can be affected.

While all nutrients cycle in ecosystems, it is through the limiting nutrient that cycling exerts regulatory feedback on productivity and other aspects of ecosystem metabolism (Pomeroy, 1970). Limitation of algal growth in streams by phosphorus, nitrogen, or both has been demonstrated in a number of studies (Huntsman, 1948; Stockner and Shortreed, 1976, 1978; Elwood et al., 1981; Bothwell, 1985; Peterson et al., 1985; Grimm and Fisher, 1986; Lohman et al., 1991; Mulholland and Rosemond, 1992; Rosemond et al., 1993; Rosemond, 1994; Wold and Hershey, 1999; Sabater et al., 2000), and there is evidence that plants can have a significant effect on stream water nutrient concentrations, especially in open stream channels with high light. Grimm (1987) found large algal uptake of nitrogen in a desert stream, and Webster et al. (2003) and Hall and Tank (2003) found that nitrogen uptake was clearly related to primary production in streams with high primary production. Similarly, a spring algal bloom in deciduous forest streams may result in decreased nutrient concentrations (eg, Hill et al., 2001).

There is also evidence that many heterotrophic microbes take up, and are limited by, nutrients. The carbon-based structural materials of vascular plant tissue, cellulose and lignin, are deficient in essential nutrients such as N and P relative to the growth needs of microbes and animals (eg, Sterner and Elser, 2002), so in order to meet their nutrient needs, some microbes associated with leaf decay take up nutrients directly from water (Kaushik and Hynes, 1968; Mathews and Kowalczewski, 1969; Triska and Buckley, 1978; Scott et al., 2013). Nutrient limitation of decomposition in streams has been widely documented (Elwood et al., 1981; Meyer and Johnson, 1983; Suberkropp and Chauvet, 1995; Pearson and Connolly, 2000; Grattan and Suberkropp, 2001; Rosemond et al., 2002; Gulis and Suberkropp, 2003; Stelzer et al., 2003; Stallcup et al., 2006; Woodward et al., 2012). Other studies have similarly related nutrient uptake to stream metabolism (Martí et al., 1997; Newbold et al., 2006; Gibson and O'Reilly, 2012; Heffernan et al., 2010; Cohen et al., 2013).

Effects of stream biota on nutrients may be most easily seen when pollution is involved. The nitrification of ammonium released from a sewage outfall produces longitudinal gradients of decreasing ammonium and increasing nitrate, as described in textbooks for water quality engineering (eg, Chapra, 1997). Reductions in stream-water nitrate attributable to denitrification were first reported in streams where an upstream enrichment from agricultural inputs (Kaushik et al., 1975), sewage inputs (Hill, 1979), or clear-cut logging (Swank and Caskey, 1982) generated a longitudinal decline in nitrate concentration. More recently, continental and global estimates of denitrification in river networks have been based largely on mass balance differences between known anthropogenic inputs and river efflux (Howarth et al., 1996; Van Breemen et al., 2002; Alexander et al., 2008; Seitzinger et al., 2010). Within-stream mass balance measurements have also implicated denitrification in a small stream receiving elevated atmospheric N inputs (Burns, 1998), but it was only with the advent of ^{15}N -based tracer studies (Böhlke et al., 2004; Mulholland et al., 2004) that estimation of denitrification in relatively pristine streams became possible.

Biotic influences can also be apparent in natural environments that are subject to temporal disturbance or longitudinal passage through a threshold. In Sycamore Creek, a desert stream in Arizona, sudden storms scour away benthic algal growths. As the benthic algae returns, nitrate is depleted from stream water, producing both longitudinal and temporal gradients in nitrate concentration (Fisher et al., 1982; Grimm, 1987). In Hubbard Brook, nitrate declined downstream after an ice storm felled trees in the upper part of the watershed (Bernhardt et al., 2003). The forest-clearing increased terrestrial nitrate input upstream, which was assimilated and denitrified downstream. In the Eel River, California, during summer low flow, dissolved organic nitrogen increased sharply downstream of a threshold stream size at which canopy opening allowed a light-stimulated proliferation of nitrogen-fixing cyanobacteria (Finlay et al., 2011). Several studies have observed diel variations in nitrogen and phosphorus concentrations and attributed these to the light-driven cycle of in-stream autotrophic activity (Manny and Wetzel, 1973; Burns, 1998; Roberts and Mulholland, 2007; Heffernan et al., 2010; Cohen et al., 2013).

Nutrient concentrations vary seasonally in many, perhaps most, streams and rivers, but interpreting such variations as a signal of in-stream biological activity can present a challenge. Seasonality in nutrient concentrations can often be ascribed to hydrological or biological control of terrestrial inputs (eg, Vitousek and Reiners, 1975; Prairie and Kalff, 1988; Goodale et al.,

2000; Kemp and Dodds, 2001; Bukaveckas et al., 2005; Brookshire et al., 2011). There are, however, reports of consistent spring and early summer declines in concentrations of dissolved phosphorus, nitrate, or both, that could clearly be ascribed, at least in part, to uptake by benthic periphyton (Webb and Walling, 1985; Casey and Clarke, 1986; Svendsen et al., 1995). Similar declines, observed after autumn leaf abscission, have been attributed to in-stream uptake of nitrogen (Goodale et al., 2009) and phosphorus (Svendsen and Kronvang, 1993) by leaf-decomposing microbes.

All of these patterns—spring and autumn declines in both nitrate and dissolved phosphorus—have been observed in intensive studies of Walker Branch, a woodland stream in Tennessee. Mulholland and Hill (1997) and Mulholland (2004) used a geochemical-based mixing model analysis to distinguish terrestrial from in-stream drivers of the seasonal variations in Walker Branch, concluding that in-stream processes caused the spring and autumn minima. Further work showed that the spring and autumn concentration minima coincided with maximum in-stream autotrophy and heterotrophy, respectively (Hill et al., 2001; Roberts et al., 2007). These were also periods of maximum nutrient retention in the stream (Roberts and Mulholland, 2007). After the spring minimum, concentrations of phosphorus and nitrogen increased sharply when the canopy closed (Hill et al., 2001).

Despite the strong evidence from Walker Branch for in-stream influences on concentrations, it remains unresolved whether, and to what degree, in-stream processes might influence seasonal dynamics in other streams and regions. For example, the summer peaks in nitrate concentration have been observed not only in Walker Branch (Lutz et al., 2012), but also in forested watersheds in North Carolina (Swank and Vose, 1997), and the upper Susquehanna River basin (Goodale et al., 2009). Yet in the latter cases, the nitrate peak has been attributed to terrestrial processes: to temperature regulation of nitrogen mineralization in the North Carolina streams (Brookshire et al., 2011) and to combined biological and hydrologic regulation of nitrogen inputs in the Susquehanna basin (Goodale et al., 2009). In more northerly and seasonally snow-covered watersheds throughout North America and Europe, nitrate concentration typically reaches a minimum, rather than a peak, during the summer (as reviewed by Goodale et al., 2009), in a pattern understood to reflect the interaction of snow-melt hydrology and nutrient demand by terrestrial vegetation (eg, Vitousek and Reiners, 1975; Williams et al., 1996).

In general, stream biota may influence the concentration of a spiraling nutrient three ways. First, nutrient may be transferred into or out of the

stream, as is the case for nitrogen fixation and denitrification, respectively. This is the only way biota affect the total long-run downstream transport of nutrient. Second, biota may alternately accumulate and lose nutrient, transiently altering concentrations from long-term or steady state averages. Finally, biota reduce the available inorganic fraction of the total nutrient transport by transforming it to transport in organic forms such as sloughed algae, suspended particles, insect drift, and dissolved organic matter. The transported organic nutrient is returned to the inorganic form through mineralization but, because the mineralization occurs downstream from the site of uptake, the steady state or long-run average concentration of inorganic nutrient is reduced. Many of the observed influences of biota on concentrations occur while nutrient standing stocks are growing or declining, yet these departures from steady state interact closely with variations among the forms (eg, dissolved inorganic versus particulate organic) in which nutrient is transported downstream. This interplay generates both temporal and longitudinal concentration dynamics that can only be described by a spatially explicit dynamic model.

Ecological stream models incorporating spiraling have been used before for organic processes (eg, Webster et al., 1979; Webster, 1983, 2007) and single nutrients (eg, Newbold et al., 1983; Newbold, 1987; Wollheim et al., 1999). In addition to spiraling, the model described in this chapter incorporates the concept of ecological stoichiometric constraints to provide the mechanism for integrating carbon and inorganic nutrient processes. In order to grow, all living organisms require a source of energy, carbon, and other elements for construction of organic tissue. Some organisms require these elements in fairly fixed proportions (chemical homeostasis), while other organisms have some flexibility in their elemental composition. Cross et al. (2005) used basic spiraling concepts to consider the effects of the stoichiometry of benthic demand on the relative uptake lengths of limiting and nonlimiting nutrients. They pointed out that these relationships could be modified by differences in the stoichiometry of inputs, such as between groundwater and leaf litter. Based on a dynamic model, Small et al. (2009) showed that the stoichiometry of microbes and consumers could strongly influence the relative downstream velocities of limiting and nonlimiting nutrients, and that these influences varied with the stoichiometric flexibility of the microbial and consumer communities. Schade et al. (2011) used field experiments to demonstrate that enrichment of the limiting nutrient (N) could enhance the uptake (shorten the uptake length) of the nonlimiting nutrient (P) where uptake was dominated by homeostatic heterotrophs, but

that this coupling was not evident where stoichiometrically flexible autotrophs dominated the uptake. Additionally, [Gibson and O'Reilly \(2012\)](#) demonstrated that seasonal variations in the stoichiometry of detritus produced corresponding variations in the stoichiometry of nutrient uptake: the influx of nitrogen-poor autumn leaves enhanced the uptake velocity of nitrogen relative to that of phosphorus. Thus, considerations of ecological stoichiometry are clearly essential to understanding biotic influences on nutrient concentration.

In this chapter, we develop a simulation model that synthesizes our understanding of in-stream processes. Our objective is to examine the influence of organisms in stream nutrient dynamics. We do this through the development of a computer simulation model that incorporates much of what we currently know about nutrient dynamics in streams, within the context of the spiraling concept and the constraints of mass balance. Thus our model includes two fundamental concepts, stream spiraling and ecological stoichiometry. It also includes both autotrophic and heterotrophic processes. In particular, we hope to provide insight into the contribution of in-stream processes to seasonal variations in nutrient concentrations.

STOICMOD—A STREAM MODEL BASED ON SPIRALING AND ECOLOGICAL STOICHIOMETRY

STOICMOD ([Fig. 1](#)) has six components—inorganic nutrients in solution in the water column, seston (organic particles in transport in the water column), decaying leaves (detritus) on the stream bottom and the microbes associated with these decaying leaves, benthic algae, and fine (<1 mm) benthic organic matter (FBOM). The decaying leaves component is further broken down into leaves and dead microbes, living microbes that obtain nutrients (N and P) only by taking it up from the water (“immobilizers”), and living microbes that obtain nutrients only from the leaves (“miners”). We realize this is an unrealistic separation of the living microbes. Many microbial species probably obtain nutrients directly from both water and from leaves, but it is important to conceptually separate these two processes. In our conceptualization, miners have more fungal-like characteristics (eg, slower maximum decay rate, lower respiration rate) than more bacteria-like immobilizers ([Table 1](#)). This separation is similar to that used by [Moorhead and Sinsabaugh \(2006\)](#) for their miners and decomposers, but our separation is based on the way microbes obtain nutrients rather than on the type of organic substrate they use.

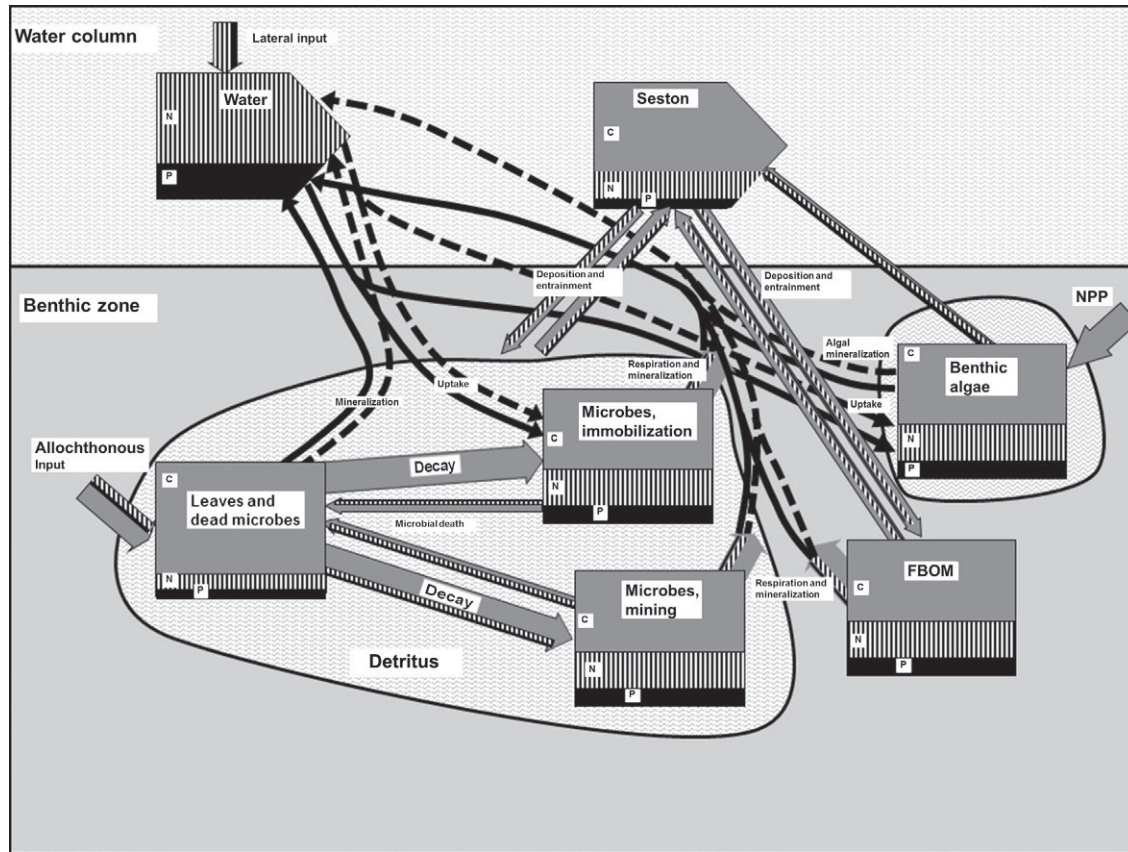


Fig. 1 Conceptual diagram of the STOICMOD model. Black is phosphorus (P), striped or dashed is nitrogen (N), and gray is carbon (C). NPP is net primary production. FBOM is fine benthic organic matter, including associated heterotrophic microbes. Detritus is coarse benthic organic matter, including leaves, large leaf particles, and living and dead microbes.

The model is stoichiometrically explicit in that state variables exist for the standing stocks of nitrogen, phosphorus, and organic carbon within each compartment (except there is no dissolved carbon in the water compartment), and transfers among compartments are mechanistically constrained by ratios of elemental abundance. In our model, we made the simplification that heterotrophic microbes are stoichiometrically homeostatic and that algae have some stoichiometric flexibility (eg, [Sterner and Elser, 2002](#)). Therefore, microbial assimilation and growth occur at fixed stoichiometric ratios, whereas algae can store limited amounts of either N or P if that element is in abundance relative to the limiting element. Various studies have shown that there is a spectrum from stoichiometrically static to large flexibility (eg, [Makino and Cotner, 2004](#); [Persson et al., 2010](#)), but the contrast of the endpoints provides a useful starting point.

Specific Fluxes

Parameter values are listed in [Table 1](#).

Downstream Fluxes

Inorganic N and P in the water and seston move downstream at the water velocity. The inorganic forms of these nutrients are soluble reactive phosphorus and totally dissolved inorganic nitrogen (=nitrate, nitrite, and ammonium). The water column concentration, C (mg/m³), of N or P is governed by the equation:

$$\frac{\partial C}{\partial t} = -\frac{\nu}{A} \frac{\partial (AC)}{\partial x} + C_g \frac{\nu}{A} \frac{\partial A}{\partial x} - U + R \quad (1)$$

where ν (m/s) is the water velocity, A (m²) is the cross sectional area, C_g is the N or P concentration of influent groundwater, U (mg/m²/s) is algal and microbial uptake, R (mg/m²/s) is algal and microbial mineralization, t (s) is time, and x (m) is downstream distance. Seston concentration (as C, N, or P) is governed by the same equation with the addition of terms for deposition and suspension.

Lateral and Upstream Nutrient Input

Lateral and upstream nutrient concentrations are low, near Redfield ratios, and similar to data for reference streams at Coweeta Hydrologic Laboratory ([Table 1](#)). There is some seasonal variability in these inputs because of seasonal variability in discharge, but concentrations were maintained constant in all simulations.

Table 1 Parameter values used in the STOICMOD simulations

Parameter	Units	Value used in autochthonous only simulations	Value used in allochthonous only simulations	Value used in simulations with both allochthonous and autochthonous energy sources
<i>Heterotrophs and detritus</i>				
Maximum leaf decay rate using leaf nutrients, $k_{\text{max-m}}$	d ⁻¹	0.0	0.01	0.01
Maximum leaf decay rate using water column nutrients, $k_{\text{max-i}}$	d ⁻¹	0.0	0.1	0.1
Miner growth C:N ratio, $(\text{C/N})_{\text{Mm}}$	Molar	N	15	15
Immobilizer growth C:N ratio, $(\text{C/N})_{\text{Mi}}$	Molar	N	5	5
Miner growth C:P ratio, $(\text{C/P})_{\text{Mm}}$	Molar	N	1000	1000
Immobilizer growth C:P ratio, $(\text{C/P})_{\text{Mi}}$	Molar	N	100	100
Miner respiration rate, r_{Mm}	d ⁻¹	N	0.05	0.05
Immobilizer respiration rate, r_{Mi}	d ⁻¹	N	0.2	0.2
Immobilizer half-saturation constant for N uptake, $k_{\text{half-NMi}}$	µgN/L	N	90	90
Immobilizer half-saturation constant for P uptake, $k_{\text{half-PMi}}$	µgP/L	N	20	20
Miner death rate	d ⁻¹	N	0.02	0.02
Immobilizer death rate	d ⁻¹	N	0.1	0.1
BOM fragmentation coefficient	d ⁻¹	N	0.01	0.01
Seston respiration/mineralization rate	d ⁻¹	0.01	0.01	0.01
Seston deposition velocity (V_{dep})	m/s	0.001	0.001	0.001
FBOM respiration-mineralization rate	d ⁻¹	0.005	0.005	0.005
FBOM entrainment coefficient	d ⁻¹	0.08	0.08	0.08

Continued

Table 1 Parameter values used in the STOICMOD simulations—cont'd

Parameter	Units	Value used in autochthonous only simulations	Value used in allochthonous only simulations	Value used in simulations with both allochthonous and autochthonous energy sources
Algae				
Maximum N uptake rate ($U_{\max-N}$)	mgN/mgC/d	0.0530	N	0.0530
Maximum P uptake rate ($U_{\max-P}$)	mgP/mgC/d	0.00731	N	0.00731
N half-saturation coefficient, $k_{\text{half-N}}$	μgN/L	14	N	14
P half-saturation coefficient, $k_{\text{half-P}}$	μgP/L	2	N	2
Self-limitation coefficient, k_s	m ² /mgC	0.0015	N	0.0015
Maximum growth rate, $G_{\max}$	d ⁻¹	1.0	N	1.0
Nitrogen subsistence cell quota, Q_{sN}	molN/molC	0.0606	N	0.0606
Phosphorus subsistence cell quota, Q_{sP}	molP/molC	0.00377	N	0.00377
Mineralization rate	d ⁻¹	0.08	N	0.08
Entrainment coefficient	d ⁻¹	0.02	N	0.02
Water nutrient concentrations				
Upstream N concentration	μgN/L	33	33	33
Upstream P concentration	μgP/L	4.4	4.4	4.4
Lateral N concentration	μgN/L	15	15	15
Lateral P concentration	μgP/L	2	2	2
Inputs				
Leaffall	gAFDM/m ² /year	0	588	250
Leaf C:N ratio	Molar	N	59	59
Leaf C:P ratio	Molar	N	3204	3204
Mean light	Lumens/m ²	4500	0	2000
Mean temperature	°C	12	12	12

Miners refers to microbial process that use leaf nutrients, and immobilizers refers to microbial processes that use nutrients directly from the water column. N, no value used for this parameter in this simulation.

Allochthonous Input

The seasonally varying input of leaf C is based on data from Hugh White Creek, Coweeta Hydrologic Laboratory (Fig. 2), and leaf N and P input are constrained by C:N and C:P ratios based on data from Cheever et al. (2013).

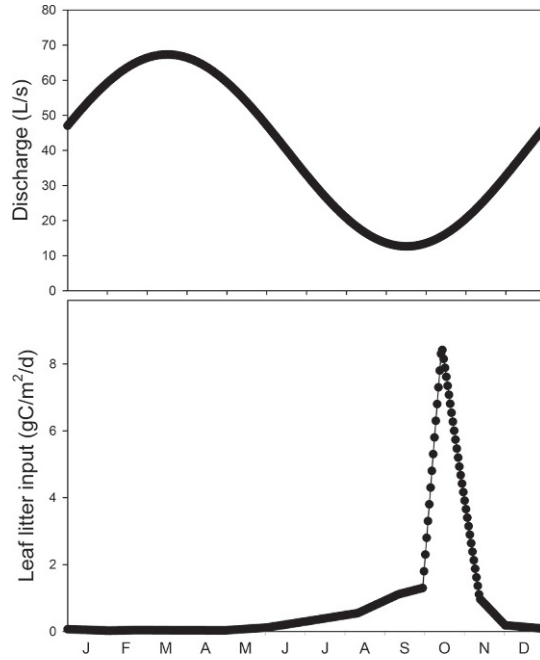


Fig. 2 Discharge (*upper panel*) and leaf litter input (*lower panel*) to a forested stream. Discharge data are for the downstream end of the 1000-m simulated stream. Leaf litter data are from Hugh White Creek, Coweeta Hydrologic Laboratory (Golladay et al., 1989; Webster et al., 2001).

Leaf Decay by Miners

This flux is similar to that used by Webster et al. (2009). Microbial assimilation of organic material is also BOM decay. The microbes responsible for BOM decay have a fixed C:N:P requirement. If nitrogen and phosphorus are in excess in the substrate relative to miner growth ratios, microbial assimilation of carbon and leaf decay (G_{Mm} , $\text{mgC}/\text{m}^2/\text{s}$) occur at the maximum rate ($k_{\text{max-m}}, \text{s}^{-1}$) modified by a Q_{10} function with a Q_{10} value of 2:

$$G_{Mm} = B_D \times k_{\text{max-m}} \times Q_{10} \quad (2)$$

where B_D is the carbon standing crop of detritus (leaves plus dead microbes, mgC/m^2).

If either nitrogen or phosphorus is insufficient in the substrate, microbial assimilation is limited by the nutrient that is least relative to the growth stoichiometry of the miners:

$$G_{Mm} = \min \left[X_D \times \left(\frac{c}{x} \right)_{Mm} \times k_{\max-m} \times Q_{10} \right] \quad (3)$$

where X_D is the detrital standing crop in terms of N or P and $(c/x)_{Mm}$ is the C:N or C:P ratio for growth of microbial miners.

The growth of miners and the equivalent decay of detritus in terms of C, N, and P are stoichiometrically related through the miner growth C:N and C:P.

Direct Mineralization

Direct mineralization of nutrients occurs when the nutrient supply in the BOM is greater than the needs of the microbial miners (ie, when the C:P or C:N of the BOM is less than the C:P or C:N requirement of the miners), the excess nutrient is released into the water column. This also occurs when one nutrient is in excess relative to the other nutrient.

Leaf Decay and Nutrient Uptake by Immobilizers

Growth of microbial immobilizers (G_{Mi} , mg/m²/s) occurs at a maximum rate modified by a Michaelis-Menten type of function (rectangular hyperbola) based on the water column concentration of the limiting nutrient:

$$G_{Mi} = (B_D \times k_{\max-i} \times Q_{10}) \times \min \left[\frac{C_x}{k_{\text{half-xMi}} + C_x} \right] \quad (4)$$

where C_x is the water column N or P concentration (mg/L) and $k_{\text{half-xMi}}$ is the half saturation constant for that nutrient for microbial immobilizers. As the immobilizers grow in terms of carbon, they also grow in terms of N and P based on the immobilizer growth C:N and C:P. These amounts of N and P are removed from the water column. However, as immobilizers use leaf C, the N and P associated with this C remains in the leaves and thus reduces the leaf C:N and C:P ratios. This provides an indirect link between microbial immobilization and microbial mining.

Respiration and Indirect Mineralization

Indirect mineralization occurs as the microbes associated with the leaves respire. Respiration is a linear function modified by a Q_{10} with a Q_{10} value of 2:

$$R_i = r_i \times B_i \times Q_{10} \quad (5)$$

where R_i is the respiration ($\text{mgC}/\text{m}^2/\text{s}$) by microbes associated with decaying leaves, seston, or FBOM; B_i is the standing crop of that compartment (mgC/m^2), and r_i is the respiration rate (s^{-1}). As they metabolize organic carbon into CO_2 , the associated nitrogen and phosphorus are released into the water column in inorganic form.

Microbial Death

Microbial death returns organic carbon, nitrogen, and phosphorus to detritus according to the elemental ratios of the microbes. Microbial death is a linear function of standing crop.

Detritus and FBOM Entrainment and Algal Soughing

Fragmentation and entrainment of detritus are treated together. That is, leaves are broken into smaller particles and entrained into the water column as seston. Entrainment of leaves and living and dead microbes are linked, that is, both living and dead microbes are part of the detritus and they are entrained together. Fragmentation/entrainment of detritus, FBOM, and algae includes organic carbon, nitrogen, and phosphorus in ratios of their respective source compartment, and they are modeled as linear functions of the respective standing crops.

Seston Entrainment and Deposition

Seston is entrained from both algae and FBOM as a linear function of the respective standing stock. Deposition is a linear function (deposition velocity) of the seston concentration. Deposited seston becomes FBOM.

Primary Production and Algal Nutrient Uptake

Algae have some stoichiometric flexibility based on the internal stores model of [Droop \(1973, 1974\)](#).

Potential algal growth rate (G_L , d^{-1}) is calculated from available light and a light response curve:

$$G_L = G_{\max} \times LRF \times L \quad (6)$$

where $G_{\max}$ is maximum algal growth rate (d^{-1}), LRF is the light response function ([Fig. 3](#), lower panel), and L is the available light ([Fig. 3](#)). Based on studies by [Boston and Hill \(1991\)](#) and [Bott et al. \(2006b\)](#), we used different light response functions for high-light and low-light adapted algae. For the high-light adapted algae, the curve approaches saturation at maximum light intensity, but for low-light adapted algae, saturation occurs at about 25% of maximum light intensity ([Fig. 3](#)).

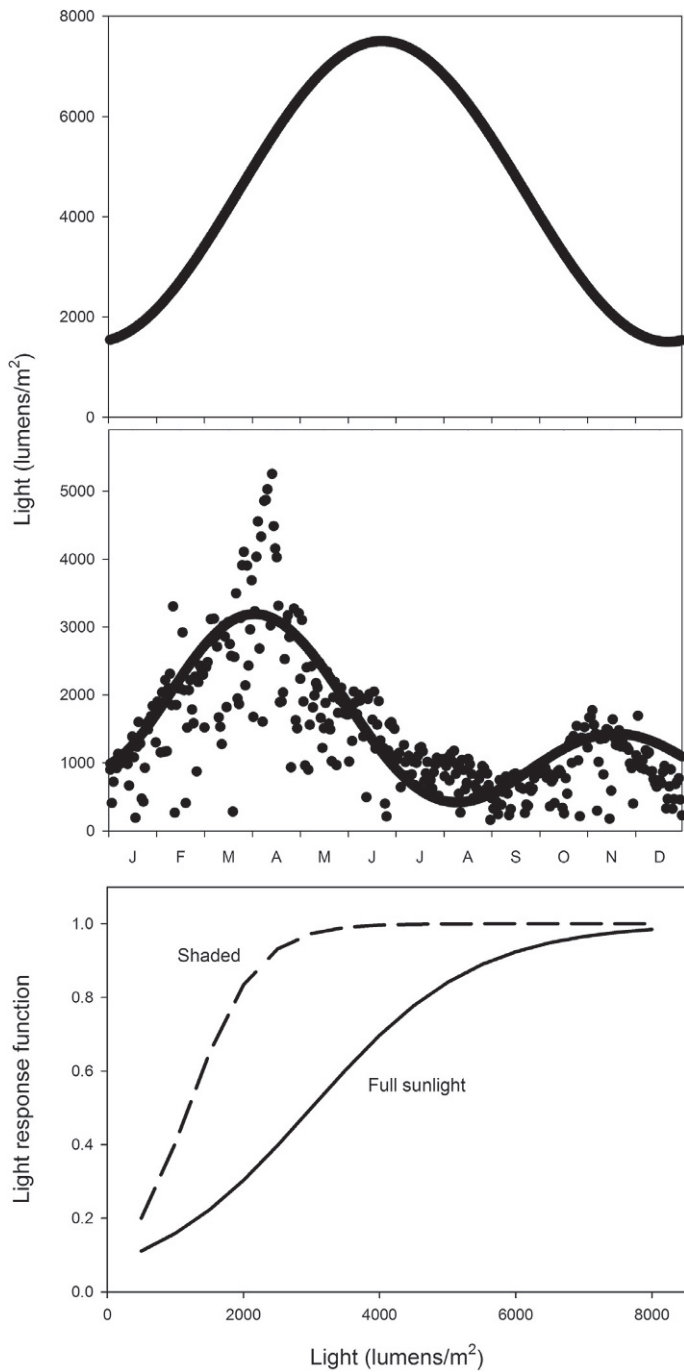


Fig. 3 Light input to unshaded (*upper panel*) and shaded (*middle panel*) streams. In the middle panel, the data are measured light for Hugh White Creek at Coweeta Hydrologic Laboratory. The lower panel shows the light response functions for algae in an unshaded stream (*full sunlight*) and a shaded stream.

Self-limitation (or biomass limitation) (g_s) of algal net primary production (NPP) is modeled as:

$$g_s = \frac{1}{1 + (k_s \times B_A)} \quad (7)$$

where k_s is a self-limitation coefficient and B_A is algal standing crop (mgC/m²).

Nutrient uptake of both N and P (mg/m²/s) is based on a Michaelis-Menten type of function modified by a Q_{10} temperature function using a Q_{10} value of 2:

$$U_x = \frac{U_{\max-x} \times C_x}{k_{\text{half}-x} + C_x} \times B_A \times g_s \times Q_{10} \quad (8)$$

where x is either N or P, $U_{\max-x}$ is the biomass specific maximum uptake (mgx/mgC/s), C_x is the water concentration of N or P (mg/m³), $k_{\text{half}-x}$ is the half-saturation constant for uptake (mg/m³), and Q_{10} is the Q_{10} function.

The internal stores limitation of NPP (g_i) is calculated as:

$$g_i = \min \left[1 - \frac{Q_{sN}}{Q_N}, 1 - \frac{Q_{sP}}{Q_P} \right] \quad (9)$$

where Q_{sx} is the subsistence cell quota (x/C ratio) for $x = N$ or P , $Q_x = B_x / B_A$ is the actual cell quota at a particular time, and B_x is the algal standing crop of x , for $x = N$ or P .

Finally, NPP (mgC/m²/s) is calculated as algal standing crop times potential algal growth rate times the limitation factors and times a Q_{10} function (Q_{10} value = 2):

$$\text{NPP} = B_A \times G_L \times g_s \times g_i \times Q_{10} \quad (10)$$

Algal Mineralization

Algal mineralization represents nutrient loss from algae by cellular exudates, death, or other processes. It is a linear function of algal standing crop modified by a Q_{10} with a Q_{10} value of 2.

Model Parameterization and Programming

Model quantification was based primarily on studies of Hugh White Creek (Coweeta Hydrologic Laboratory), White Clay Creek (Stroud Water Research Lab, Pennsylvania, USA), Walker Branch (Oak Ridge National Laboratory, Tennessee, USA), and other streams in those areas. Nominal

parameter values (Table 1) are typical values derived from our past research or assigned to achieve realistic initial simulations. Our simulations were based on a 1000-m stream reach, 1-m wide upstream, and increasing linearly to 3 m downstream. Discharge varied seasonally (Fig. 2) with a mean upstream discharge of 10 L/s and downstream of 40 L/s. Velocity was constant over the reach at 10 cm/s, and depth was calculated from width, velocity, and discharge. We ran the model for two years, the first year to stabilize standing stocks, and we then based our results on year 2. Temperature varied as a sinusoidal function with a nominal mean of 12°C with maximum and minimum occurring on the summer and winter solstices. For unshaded model simulations, solar input was also sinusoidal with a peak in mid-Jul. For shaded streams, we fit a function to data from Hugh White Creek with a peak in early Apr. and a smaller peak in mid-Nov. (Fig. 3).

The model was programmed as hundred 10-m stream segments. Within each segment, all state variables were dynamically updated using the Euler integration technique every 10 s. After each dynamic integration step, water column variables were moved downstream one segment and diluted based on the increase in discharge and the concentrations of incoming groundwater. The upstream water column segment was reset to initial values. The model was programmed in C++ and executed using ABSOFT software (ABSOFT Corporation, 2781 Bond Street, Rochester Hills, Michigan, USA) with a DISLIN user interface (DISLIN Scientific Plotting Software, Max Planck Institute for Solar System Research, Lindau, Germany).

SIMULATIONS

In addition to examining seasonal dynamics of standing crops and various fluxes, we used our model to calculate many annual values and averages (Tables 2 and 3). Unless otherwise noted, all of our results are presented for the downstream end of the 1000-m reach or, as in the case of net uptake, for the total for the whole reach. Of particular note is the annual net uptake, which is the total annual algal and microbial uptake within the reach, less algal and microbial mineralization. We report annual net uptake as percent of the dissolved nutrient input. It thus represents the reduction in dissolved inorganic nutrient export relative to upstream and lateral dissolved inputs. Reductions in dissolved inorganic nutrient concentrations have sometimes been reported as “retention,” reflecting the short-term uptake of nutrient on the streambed (eg, Peterson et al., 2001). We prefer “net uptake” because in the long-run (specifically, year-to-year), all net uptake is exported

Table 2 Results of STOICMOD simulations

	Autoch- thonous only	Alloch- thonous only	Combined model (default)	Combined model with 2°C increase	Combined model with 4°C increase	Combined model with 10 µg/L increase in lateral N input	Combined model with 25 µg/L increase in lateral N input	Combined model with 2 µg/L increase in lateral P input	Combined model with 10 and 2 µg/L increase in lateral N and P
NPP (gC/m ² /year)	98.1	0	41.4	50.7	61.1	41.7	41.7	41.1	47.7
NEP (gC/m ² /year)	−0.03	−123.9	−57.3	−61.8	−66.5	−57.2	−57.2	−60.8	−62.6
Net N uptake (%)	26.3	18.5	25.9	23.8	21.6	20.2	15.2	28.3	24.8
Net P uptake (%)	27.9	22.8	27.9	27.0	26.1	28.2	28.2	20.6	23.2
C:N of seston (molar)	11.1	28.9	19.9	19.7	19.5	19.2	18.6	18.6	16.6
C:P of seston (molar)	206.9	896.8	489.3	477.6	465.9	487.1	487.1	425.4	382.8
Decay rate (d ^{−1})	—	0.0182	0.0193	0.0200	0.0207	0.0193	0.0193	0.0207	0.0216
Miner assimilation (gC/m ² /year)	0	47.5	22.0	23.6	25.1	22.0	22.0	22.4	23.1
Immobilizer assimilation (gC/m ² /year)	0	57.2	31.2	31.3	31.4	31.0	31.0	38.0	44.4

NPP is net primary production and NEP is net ecosystem production. Decay rate is the exponential decay rate of CBOM from 1 Dec. to 31 Mar.

Table 3 N:P ratios (molar) from STOICMOD simulations

	Autoch- thonous only	Alloch- thonous only	Combined model (default)	Combined model with 2°C increase	Combined model with 4°C increase	Combined model with 10 µg/L increase in lateral N input	Combined model with 25 µg/L increase in lateral N input	Combined model with 2 µg/L increase in lateral P input	Combined model with 10 and 2 µg/L increase in lateral N and P
Lateral water input	16.6	16.6	16.6	16.6	16.6	27.7	44.3	8.3	13.8
Microbial immobilization	–	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0
Algal uptake	17.3	–	17.0	17.1	17.2	20.0	22.8	13.5	15.9
Total uptake	17.3	20.0	18.1	18.0	17.9	20.0	21.8	15.7	17.2
Microbial mineralization	18.7	22.3	21.2	21.3	21.3	21.5	21.7	20.6	20.6
Total mineralization	17.4	22.3	18.7	18.6	18.5	20.5	22.3	16.2	17.6
Algal biomass	17.2	–	17.0	17.1	17.2	20.3	23.3	13.2	15.5
Seston	18.6	31.0	24.6	24.1	23.9	25.2	26.1	22.6	22.9

These results are all for the downstream end of the 1000-m reach. Input values used in the simulations were: leaf N:P = 54.3, miner growth N:P = 66.7, immobilizer growth N:P = 20, algal maximum uptake, half-saturation, and subsistence cell quota N:P = 16.0.

as dissolved organic or particulate nutrients (ie, none is actually retained in the reach). On shorter (<1 year) time scales, temporary retention occurs during periods of high net uptake and accumulating biomass, but these are offset by periods of net mineralization and declining biomass.

Simulations With Autotrophic Model Components Only

To simulate a stream with only autochthonous energy inputs, we used a fairly high solar input (Table 1) with peak sunlight at the summer solstice (Fig. 3, upper panel). NPP was very low during the winter, but increased rapidly in spring, reaching maximum value with maximum sunlight (Fig. 4). Algal biomass mirrored this pattern. Annual NPP was $98.1 \text{ gC/m}^2/\text{year}$. This is fairly typical compared to results from a study recently completed in small streams in the upper Little Tennessee River watershed in which NPP ranged from 23.5 to $100 \text{ gC/m}^2/\text{year}$ in partially open-canopy streams (Hart, 2013). We calculated annual NPP of $157 \text{ gC/m}^2/\text{year}$ for open canopy streams in Pennsylvania from the study by Bott et al. (2006b) and a range of 16 – $296 \text{ gC/m}^2/\text{year}$ for streams in New York (Bott et al., 2006a).

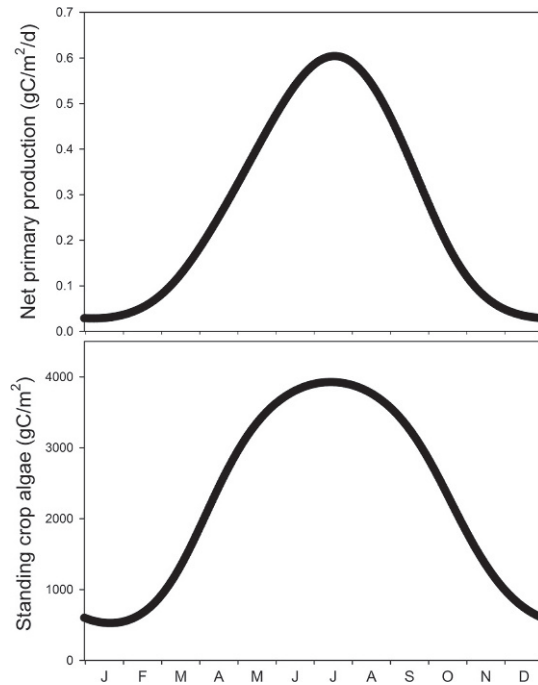


Fig. 4 Net primary production (*upper panel*) and algal standing crop (*lower panel*) from the simulation with full sunlight and no leaf fall input.

Autotrophic uptake of dissolved nutrients resulted in a strong reduction in both N and P during summer (Fig. 5). We have no actual stream data for direct comparison to these results, because open-canopy streams with low nutrient inputs do not exist in eastern United States. Generally, where riparian canopy has been removed from small streams, it was to clear land for agriculture, which also resulted in elevated nutrient inputs. For example, most of the riparian vegetation has been removed from along Skennah Creek in Macon Co., North Carolina, and the stream receives elevated nitrogen inputs from agricultural and residential areas (Webster et al., 2012). However, the seasonal pattern of nitrate in this stream illustrates the summertime autotrophic removal of dissolved inorganic nitrogen (Fig. 5).

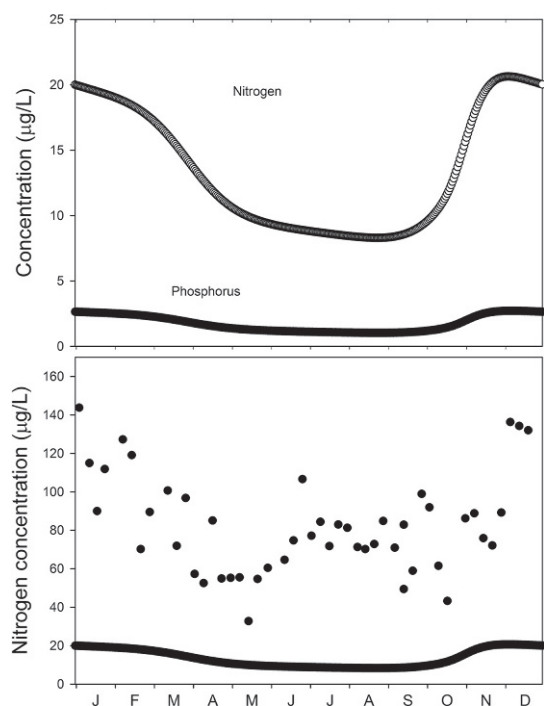


Fig. 5 Nitrogen and phosphorus concentrations (*upper panel*) from the simulation with full sunlight and no leaf fall input. In the lower panel, simulated nitrogen concentration is compared with data for nitrate (mgN/L) from Skennah Creek, an open-canopy stream in Macon Co., North Carolina, near Coweeta Hydrologic Laboratory. Data points are weekly grab samples from 2010 and 2011 (Webster and others, unpublished).

In our autotrophic-only simulation, algae became more nutrient limited and more nutrient depleted (higher C:N and C:P ratios) during the growing season (Fig. 6). Also, algae appeared to be more P limited as they became more nitrogen rich when they were most actively growing. However, this

was because the nutrient supply in lateral inputs (Table 1) was slightly richer in N ($N:P = 16.6$) than the Redfield ratio ($N:P = 16.1$). Uptake of both N and P always exceeded mineralization so that there was always net uptake of both nutrients (Fig. 7). Annually, there was a net uptake of 26.3% of input dissolved N and 27.9% of dissolved P within the 1000-m reach (Table 2). The net uptake was exported as seston. Because the seston generated within the reach was entirely from sloughed algae, it was much more nutrient rich (molar $C:N = 11.1$; molar $C:P = 206.9$, Table 2) than the upstream input (molar $C:N = 59.0$; molar $C:P = 3203$).

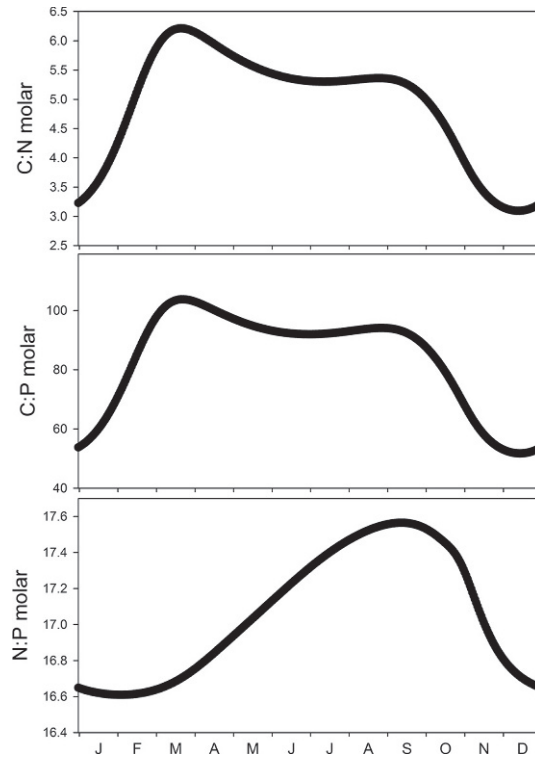


Fig. 6 Molar ratios of algae from the simulation with full sunlight and no leaf fall input.

Simulations With Heterotrophic Model Components Only

In our second simulation, we changed inputs to represent a stream with a heavy riparian forest cover—no solar input, no autochthonous production, and a large autumn input of leaves (Table 1). The results fairly closely matched measurements made in streams at Coweta Hydrologic Laboratory. FBOM and CBOM (coarse benthic organic matter) were similar to

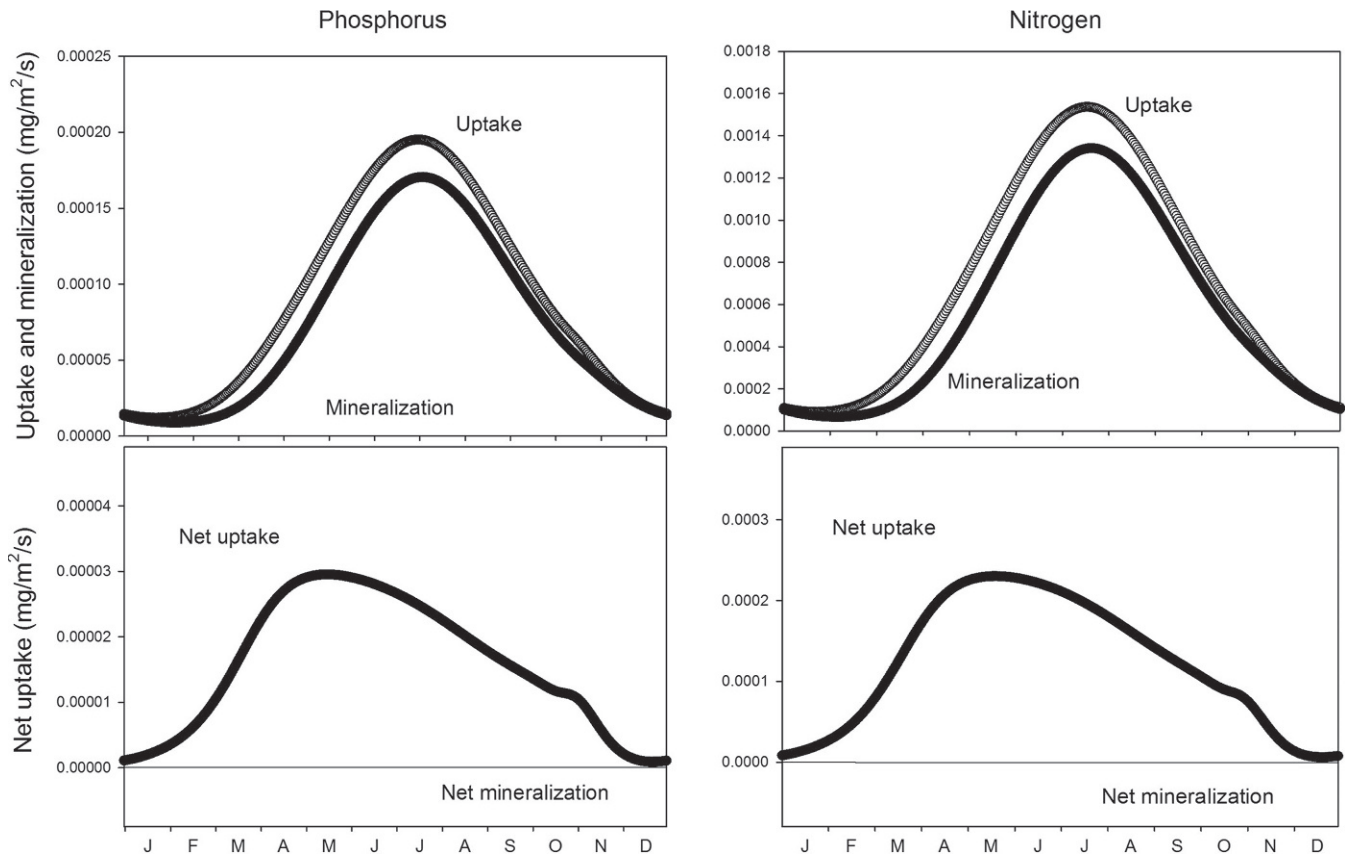


Fig. 7 Phosphorus (*left panels*) and nitrogen (*right panels*) uptake, mineralization, and net uptake from the simulation with full sunlight and no leaf fall input. For both nutrients, uptake always exceeded mineralization, so net uptake was always positive.

measured values in both magnitude and seasonal variability (Fig. 8). Over the course of a year, live microbes averaged 5.3% of CBOM C (Fig. 8) and 16.0 and 16.5% of CBOM N and P. Dead microbial tissue averaged 8.1% of C, 42.5% of N, and 59.4% of P, with maximum values of 40.1%, 70.3%, and 86.8% in late spring.

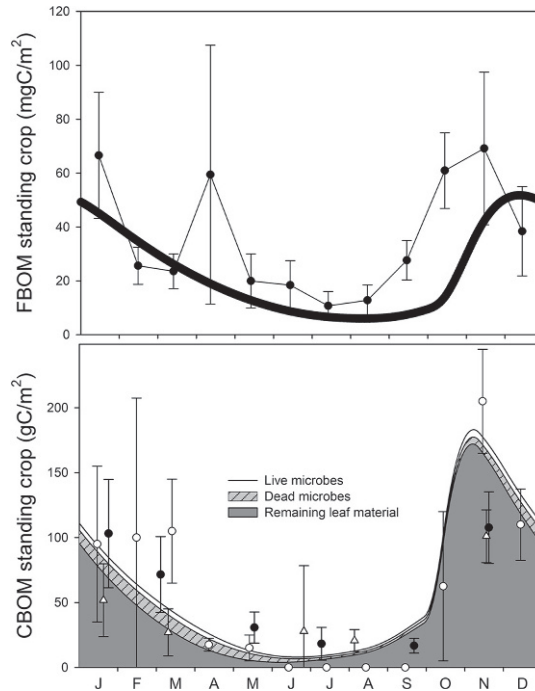


Fig. 8 Fine benthic organic matter (FBOM, *upper panel*) and coarse benthic organic matter standing crop (CBOM, *lower panel*) from the simulation with no primary production and full leaf input. In the upper panel, the data are means with standard error bars for reference streams at Coweeta Hydrologic Laboratory (D'Angelo and Webster, 1991). In the lower panel, the data points are also from measurements in reference streams at Coweeta Hydrologic Laboratory: Solid circle data points are from Webster et al. (2001) with 95% error bars, the open circles are from D'Angelo and Webster (1991) with standard error bars, and the open triangles are from Hugh White Creek (Webster and others, unpublished, 2012–13) with 95% error bars. For all data points, we estimated AFDM as 50% carbon.

We did not use a microbial net production efficiency (or carbon use efficiency or net growth efficiency) in our model (eg, as used by Manzoni et al., 2008, 2010), but rather we calculated assimilation and respiration separately. The microbial net production efficiency produced in our simulations ranged from 25% to 55%, and was largely influenced by temperature

effects on respiration and the organic matter supply (ie, lowest values in summer with high temperature and low organic matter available). This is consistent with the meta-analysis by [del Giorgio and Cole \(1998\)](#). Net production efficiencies for river microbes ranged from 3% to 46% and were lowest when the organic matter supply was lowest.

As leaves were conditioned, that is, colonized by microbes ([Cummins, 1974](#); [Bärlocher and Kendrick, 1975](#)), C:N and C:P ratios declined, reaching minimum values (maximum nutrient content) in late spring, and then increased through autumn with input of fresh, less nutrient rich leaf litter ([Fig. 9](#)). As a result of this heterotrophic microbial uptake of nutrients by the microbes associated with decaying leaves, dissolved inorganic N and P in the water column declined in late summer and fall and were lowest in early winter and highest in summer when there was very little leaf tissue remaining in the stream ([Fig. 10](#)). Our results are generally similar to measured dissolved nutrient concentrations from streams at Coweeta Hydrologic

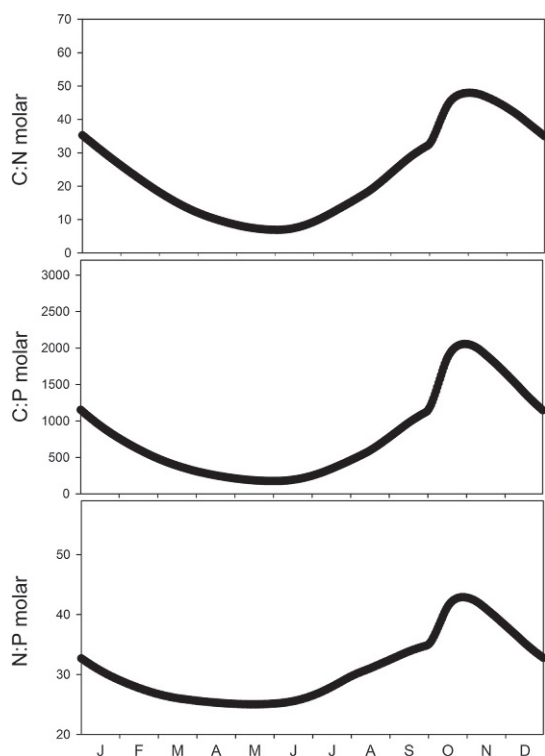


Fig. 9 Molar ratios of coarse benthic organic matter including live and dead microbes from the simulation with no primary production and full leaf input. In each panel, the top of the vertical axis is the ratio for leaves falling into the stream.

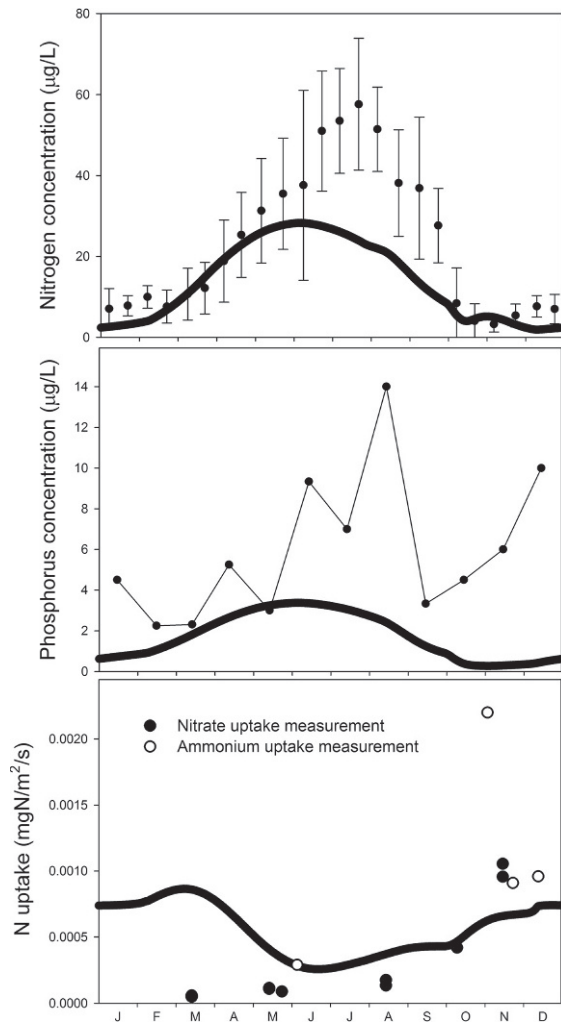


Fig. 10 Nitrogen (*upper panel*) and phosphorus (*middle panel*) concentrations and nitrogen immobilization (*lower panel*) from the simulation with no primary production and full leaf input. The data in the upper panel are nitrate nitrogen in Hugh White Creek, means and standard errors from bi-weekly grab samples, 2005–08 (US Forest Service). In the middle panel, the data are monthly means of weekly grab samples of soluble reactive phosphorus from Ball Creek, Coweeta Hydrologic Laboratory, 2010–11 (Webster and others, unpublished data). The data points in the lower panel are ^{15}N -measured nitrate or ammonium uptake in streams at Coweeta Hydrologic Laboratory: Hugh White Creek (Hall et al., 1998; Earl et al., 2006; Mulholland et al., 2008), Hugh White Creek and Snake Den Branch (Valett et al., 2008), Upper Ball Creek (Tank et al., 2000).

Laboratory, though the data suggest that the concentration decline occurs more precipitously in early autumn rather than beginning in early summer. Studies of Walker Branch also suggest a fairly precipitous decline in P and N coincident with leaf fall (Mulholland and Hill, 1997; Lutz et al., 2012). The differences between data and our simulations may have to do with seasonal variation in lateral (terrestrial) input concentrations, which was not included in our simulations.

For both N and P, uptake exceeded mineralization, so that there was net uptake through much of the year (Fig. 11). However, during spring through mid-summer, mineralization was greater than uptake and there was net mineralization (Fig. 11). Annually, net uptake was 18.5% for N and 22.8% for P for the 1000-m reach. Our simulation of N uptake was within the range of measurements of N uptake made in Coweeta streams, though somewhat higher through most of the year and lower in autumn (Fig. 10, lower panel). The only published, isotope-measured uptake of P in Coweeta streams was made by Mulholland et al. (1997). They measured P uptake of $0.148 \mu\text{g}/\text{m}^2/\text{s}$ in Jul., compared to our simulation of about $0.02 \mu\text{g}/\text{m}^2/\text{s}$ at that time of year (Fig. 11). In the same study, they measured P uptake in Walker Branch of $0.06 \mu\text{g}/\text{m}^2/\text{s}$ (Mulholland et al., 1997).

Over the year, the contributions of miners and immobilizers to leaf decay was very similar; immobilizers contributed 54.6% of total annual leaf decay (= microbial assimilation) and miners contributed 45.4%. However, their role in leaf decay varied over the year (Fig. 12). Most miner assimilation occurred in autumn, whereas immobilizer assimilation peaked in winter. If miners are primarily fungi and immobilizers are primarily bacteria, this pattern is consistent with the generally accepted pattern of initial fungal colonization and later bacterial colonization of leaves (eg, Suberkropp and Klug, 1976; Kuehn et al., 2000).

In order to evaluate possible interactions between miners and immobilizers, we ran two modifications of the allochthonous-only model to eliminate interactions. In the first simulation, leaf nutrients associated with the use of leaf C by immobilizers were released into the water rather than accumulated in the leaves. In the second simulation, miner mineralization simply disappeared rather than go into the water column. Both simulations showed significant interactions (Fig. 13). Without immobilizer-generated leaf nutrients, miner assimilation was lower and the miner decay rate was slower, especially in late summer. In the same way, without miner mineralization, immobilizer assimilation was lower throughout most of the year and immobilizer decay was slower through spring and summer.

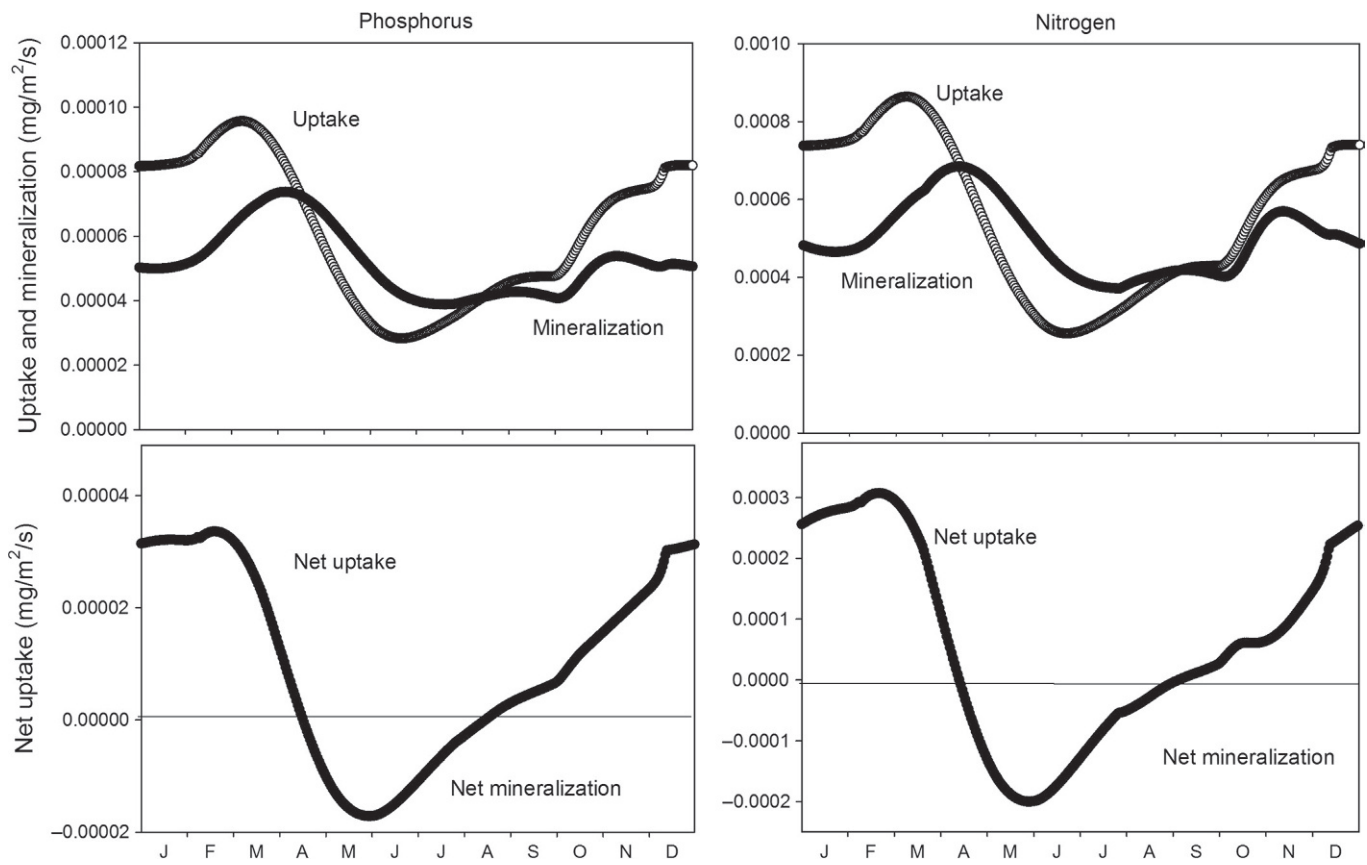


Fig. 11 Phosphorus (*left panels*) and nitrogen (*right panels*) uptake, mineralization, and net uptake from the simulation with no primary production and full leaf input. For both nutrients, there were periods of positive net uptake and net mineralization.

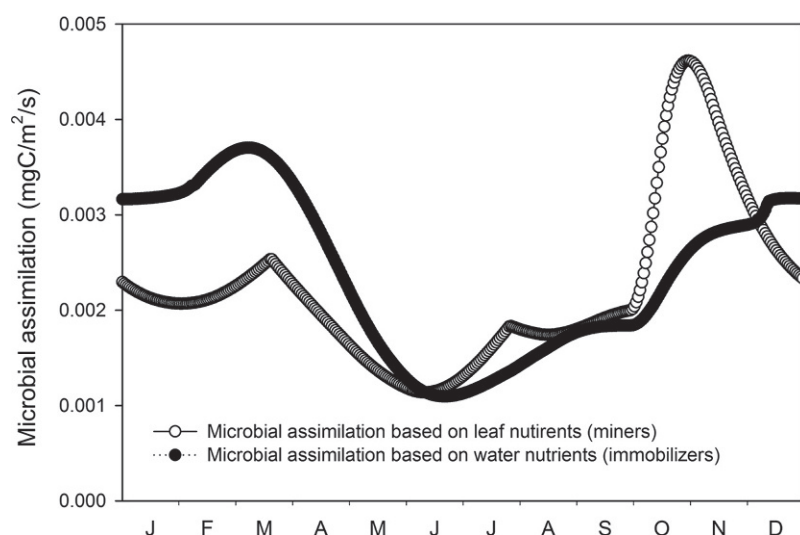


Fig. 12 Microbial assimilation by miners and immobilizers from the simulation with no primary production and full leaf input.

Simulations With Both Autochthonous and Allochthonous Energy Inputs

In the next simulations, we included both algal photosynthesis and leaf fall to simulate a stream with both sources of energy. Total light input was lower than the autochthonous-only simulation (Table 1), but was shifted to represent light input to a stream that is mostly shaded in summer and receives maximum light in spring (Fig. 2, middle panel). Also, the light response function was changed to characterize more low-light adapted algae (Fig. 2, lower panel). Similarly, leaf input was reduced to less than half that of a fully canopied stream (Hagen et al., 2010; Table 1).

With lower light input, NPP was less than one-half of that in the autochthonous-only simulation (Table 2), and the stream was strongly heterotrophic, with a large peak in ecosystem respiration coinciding with primary production and a smaller peak in autumn with leaf fall (Fig. 14). Seasonal trends in uptake and net uptake followed this same pattern (Fig. 15). Our simulated uptake was within the range of ^{32}P -measured P uptake in Walker Branch (Mulholland et al., 1985; Fig. 16, lower panel). The Walker Branch data suggest even greater seasonal variability, with peaks in late winter-spring and autumn. The resulting pattern of dissolved nutrient concentration had two peaks (Fig. 16, upper panel), similar to what has been observed for streams with both significant autochthonous and allochthonous inputs

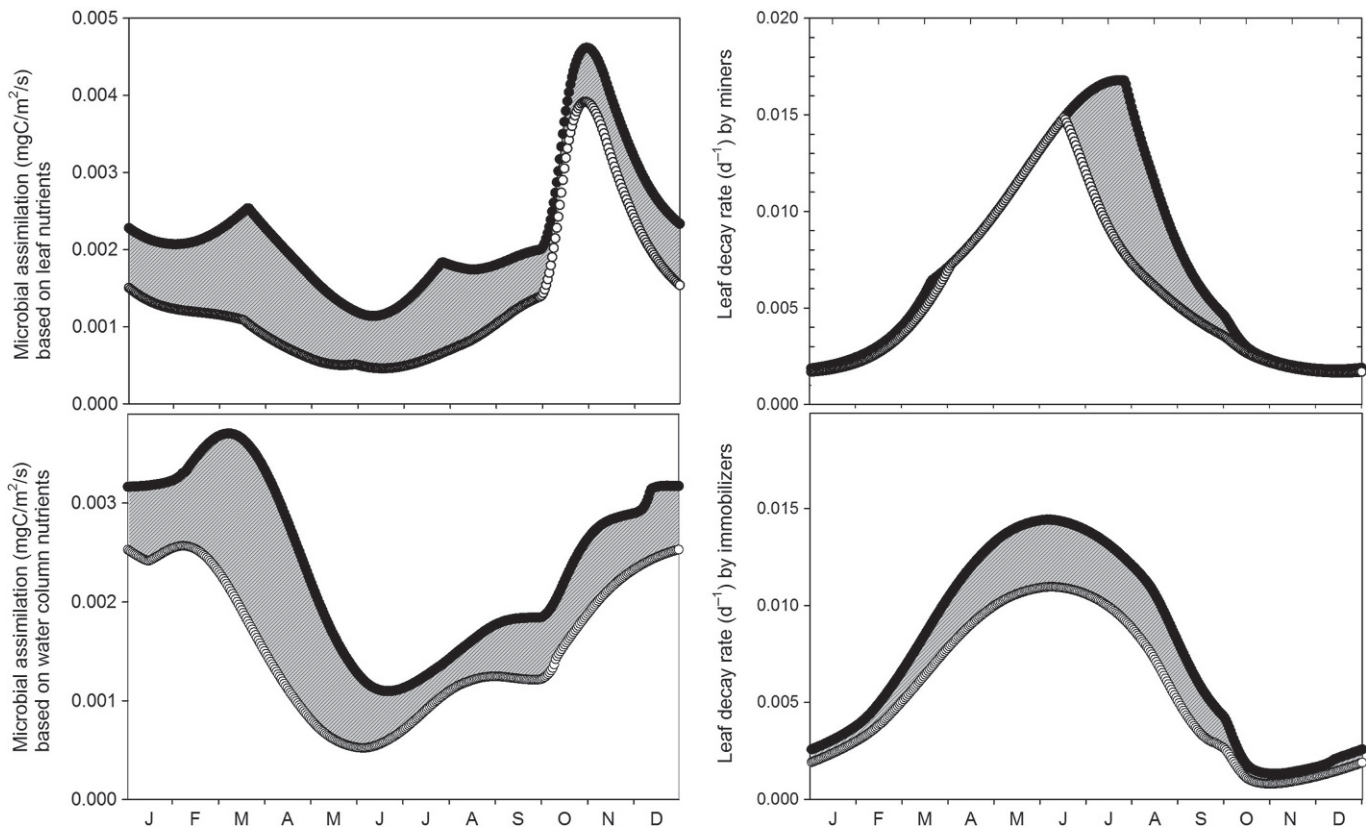


Fig. 13 Microbial assimilation (*left panels*) and leaf decay rate (*right panels*) from the simulation with no primary production and full leaf input. The upper panels are production and decay by miners, and the lower panels are assimilation and decay by immobilizers. In each panel, the upper line (*closed circles*) represents the default simulation. In the upper panels, the lower line is a simulation in which the leaf nutrients associated with immobilizer decay were released to the water column rather than accumulated in the detritus. In the lower panels, the lower lines are from a simulation in which nutrients released by mineralizers were simply lost and did not go into the water column. In each panel, the gray area represents the assimilation or decay rate based on nutrients supplied by the other microbes.

(eg, Walker Branch, Lutz et al., 2012). Annual net uptake for both N (25.9%, Table 2) and P (27.9%) was similar to the autochthonous-only simulation and similar to Walker Branch (20% N, 30% P, Mulholland, 2004).

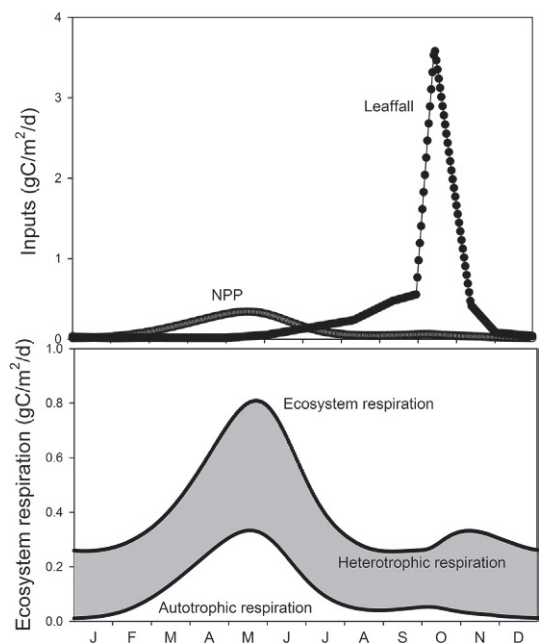


Fig. 14 Inputs to the stream for the simulation including both autochthonous and allochthonous inputs (*upper panel*). The lower panel shows ecosystem respiration (*top line*) partitioned into heterotrophic (*gray area*) and autotrophic respiration (*white area*). Autotrophic respiration was estimated as equal to NPP (50% of gross primary production).

We also found that the CBOM decay rate was slightly greater than the allochthonous-only simulation (Table 2), possibly because dissolved nutrient concentrations were higher in winter (compare Figs. 10 and 16) when most decay was by immobilizers (Fig. 12).

The focus of this chapter is the effects of biota on nutrient concentrations; however, to support the usefulness of our model, we evaluated spiraling metrics (uptake and turnover lengths, exchange and transport fluxes, and uptake velocities) for the combined model. At the downstream end of the reach, annual average uptake, U , was 21.4 gN/m²/year and 2.59 gP/m²/year. Downstream dissolved flux, F_w , was 18,250 gN/year and 2350 gP/year. With a stream width, w , of 3 m, the average uptake length, $S_w = F_w / (U \times w)$ (Newbold et al., 1982), was 284 m for nitrogen and 303 m for phosphorus. The uptake velocity, $v_f = v \times d / S_w$, where v is water velocity and d is depth

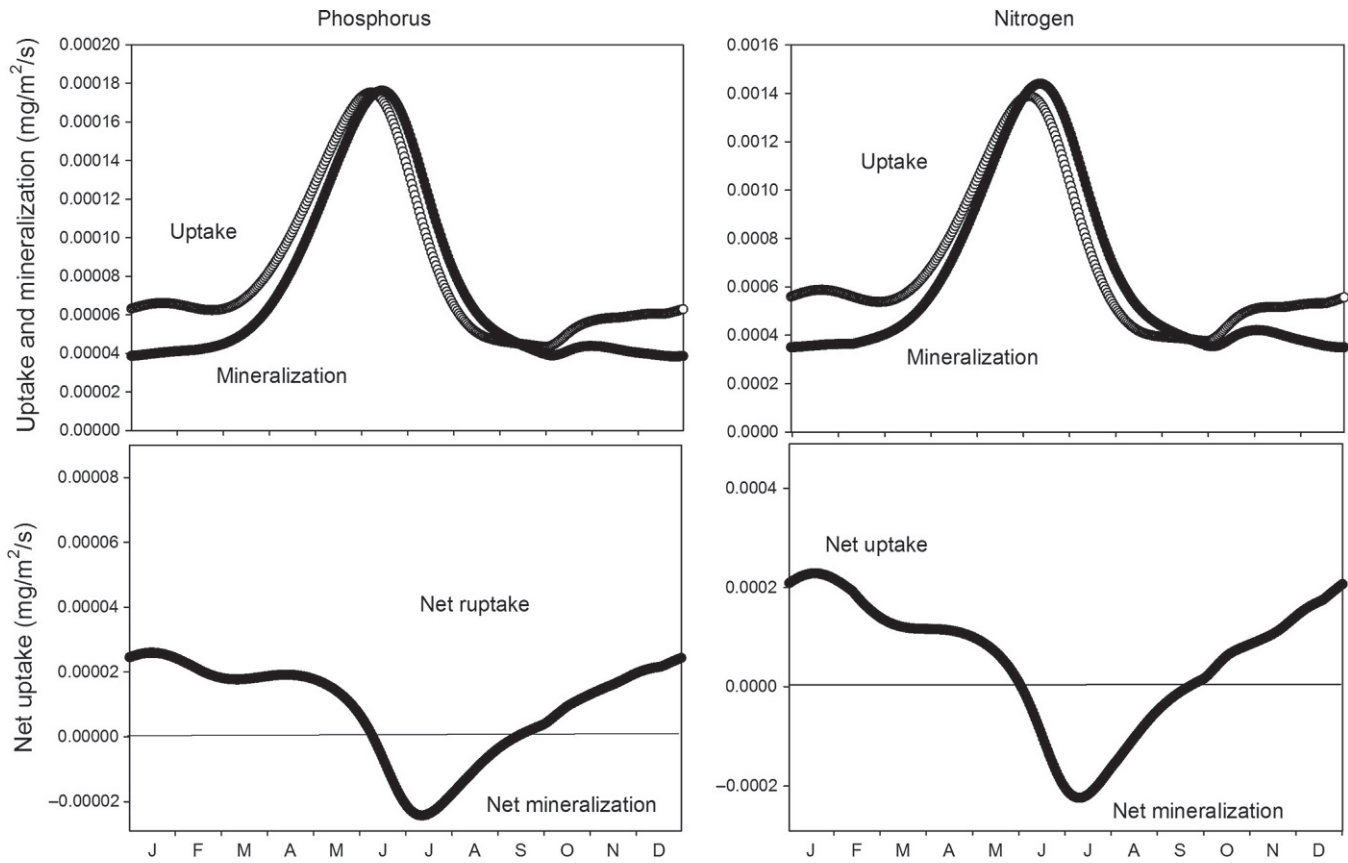


Fig. 15 Total phosphorus (*left panels*) and nitrogen (*right panels*) uptake, mineralization, and net uptake for the simulation, including both autochthonous and allochthonous inputs. For both nutrients, net uptake was positive for most the year but with a period of net mineralization in the summer.

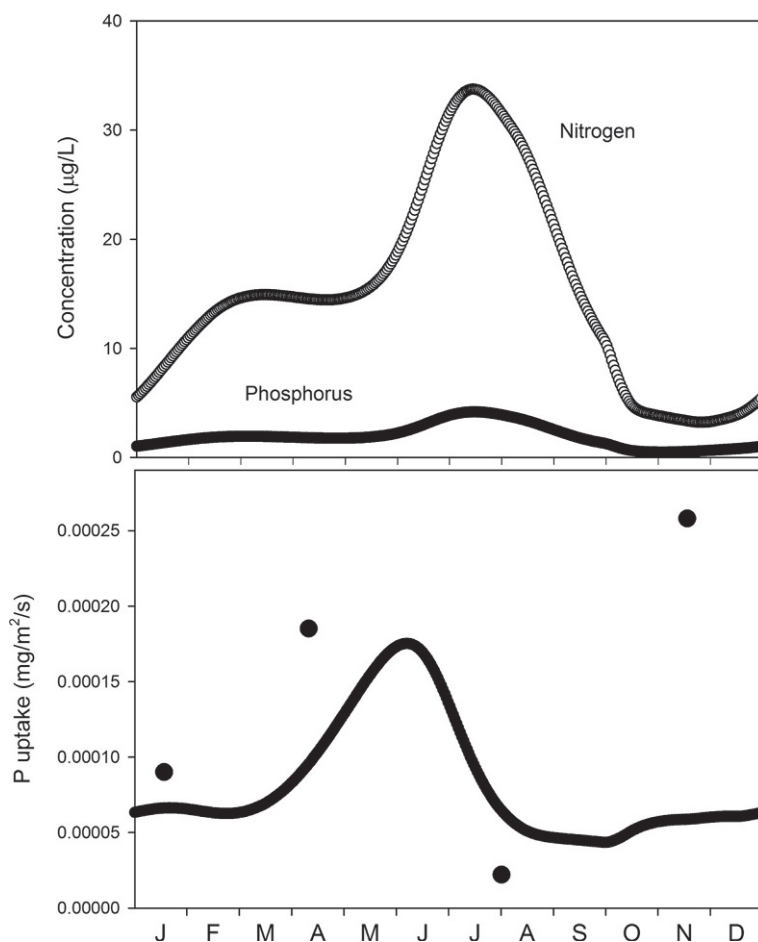


Fig. 16 Nitrogen (open circles) and phosphorus (closed circles) concentrations (top panel) and P uptake (lower panel) for the simulation, including both autochthonous and allochthonous inputs. The data points in the lower panel are from Walker Branch (Mulholland et al., 1985).

(Stream Solute Workshop, 1990), was 0.047 mm/s for N and 0.044 mm/s for P. These values fall within the ranges reported by Ensign and Doyle (2006) for second-order streams.

Mineralization flux, R , was 19.8 gN/m²/year and 2.31 gP/m²/year. Downstream seston flux, F_B , was 13,250 gN/year and 1210 gP/year, giving turnover lengths, $S_B = F_B / (R \times w)$, of 223 and 175 m for N and P, respectively. The total spiraling lengths, $S = S_W + S_B$, then were 507 and 478 m for N and P, respectively. They were somewhat shorter upstream (data not presented) than downstream, as is typical of spiraling lengths (Ensign and Doyle, 2006;

Hall et al., 2013). The similar lengths for N and P reflect the approximate stoichiometric balance of the inputs. Thus nutrients entering at or near the upstream end of the reach were cycled more than twice within the 1000-m reach. Mineralization was less than uptake ($U < R$) for both N and P by relatively small amounts (7% and 11%, respectively), this difference accounting for the annual average net uptake of N and P from the water and the longitudinal increase in seston flux.

Both S_w and S_b varied throughout the year, with our model showing that the ratio S_b/S reached minima of 0.26 for N and 0.23 for P in Jul. when nutrient concentrations were high and conversion to seston was low. Newbold et al. (1981, 1983) estimated S_b/S at 0.13 for P in Walker Branch, Tennessee, in Jul. and early Aug. Studies have cited the Walker Branch estimate (the only published estimate that we are aware of) as evidence that S_b is short, so that S_w reasonably approximates S (eg. Stream Solute Workshop, 1990; Ensign and Doyle, 2006), but our model suggests that the Walker Branch estimate was an annual minimum that substantially underestimated the annual average ratio of S_b/S .

To determine possible interactions between autotrophic and heterotrophic organisms, we repeated this simulation in four ways: (1) with no light to eliminate autotrophic processes, so there was no competition for nutrients between autotrophs and heterotrophs, and there was no regeneration of algal-fixed nutrients; (2) with light, but with no algal-fixed nutrient regeneration; (3) with no leaf fall to eliminate heterotrophic processes; and (4) with leaf fall, but no mineralization of leaf nutrients. In general the results showed competition for nutrients between autotrophs and heterotrophs during some times of the year (Fig. 17). Without competition from heterotrophic immobilizers, NPP was substantially increased in summer and fall, but through winter and spring, a large fraction of NPP was based on leaf-derived nutrients. Similarly, when there was no primary production, leaf decay rate increased in spring, but without regeneration of algal-fixed nutrients, leaf decay rate was slowed through most of the growing season (Fig. 17).

Climate Change Experiments

Using the simulation with both autochthonous and allochthonous inputs, we ran two series of experiments to investigate possible results of climate change. In the first series, we increased temperature by 2°C and then by 4°C. In the second series, we increased nutrient levels: we increased dissolved inorganic nitrogen by 10 µg/L and then by 25 µg/L; we then increased P by 2 µg/L and then N by 10 and P by 2 µg/L.

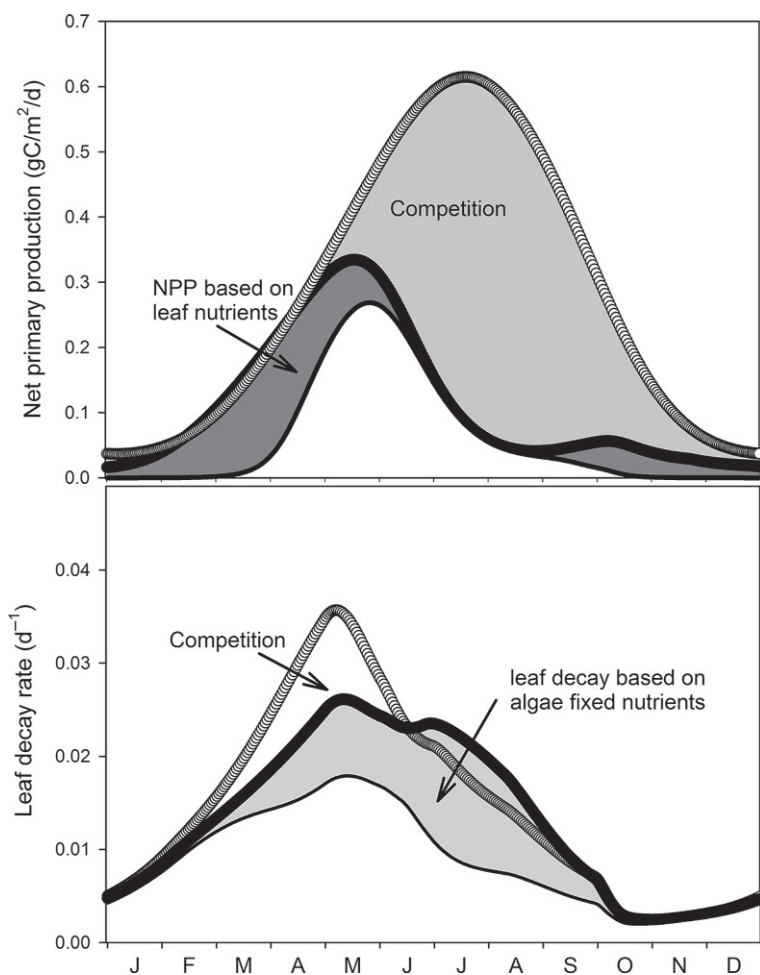


Fig. 17 Interactions of autochthonous and allochthonous processes for the simulation, including both autochthonous and allochthonous inputs. In both panels, the heavy line (*closed circles*) is the default simulation with both algae primary production and allochthonous leaf input. In the upper panel, the line with open circles is a simulation with no leaf input, and the thinner line is a simulation with leaf input, but no regeneration of leaf nutrients either through leaf mineralization or fragmentation and FBOM mineralization. In the lower panel, the line with open circles is a simulation with no light and therefore no primary production, and the thinner line is a simulation with primary production, but no regeneration of algae-immobilized nutrients either by algae mineralization or by algal sloughing and FBOM mineralization.

Results of Elevated Temperature

Elevated temperature increased both NPP and the leaf decay rate (Fig. 18 and Table 2). Despite increased NPP and autotrophic uptake in summer, increased mineralization resulted in slightly higher N concentration (Fig. 19). Increased leaf decay rate was primarily due to greater miner assimilation (Fig. 19 and Table 2). Immobilizer assimilation was elevated in fall but reduced in winter and spring (Fig. 19). Both N and P net uptake was reduced at higher temperatures (Table 2) because temperature affects mineralization

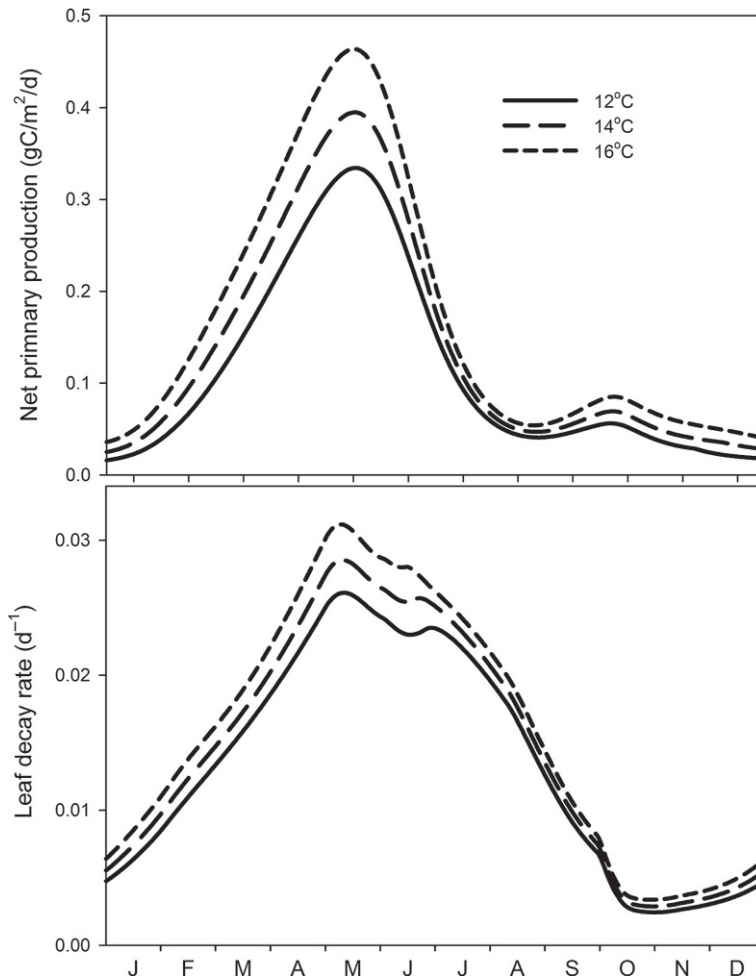


Fig. 18 Results of 2°C and 4°C temperature increases on net primary production (*upper panel*) and leaf decay rate (*lower panel*). These results are from simulations of the model with both autochthonous and allochthonous inputs.

directly, whereas both autotrophic and heterotrophic uptake are primarily limited by availability of inorganic nutrients.

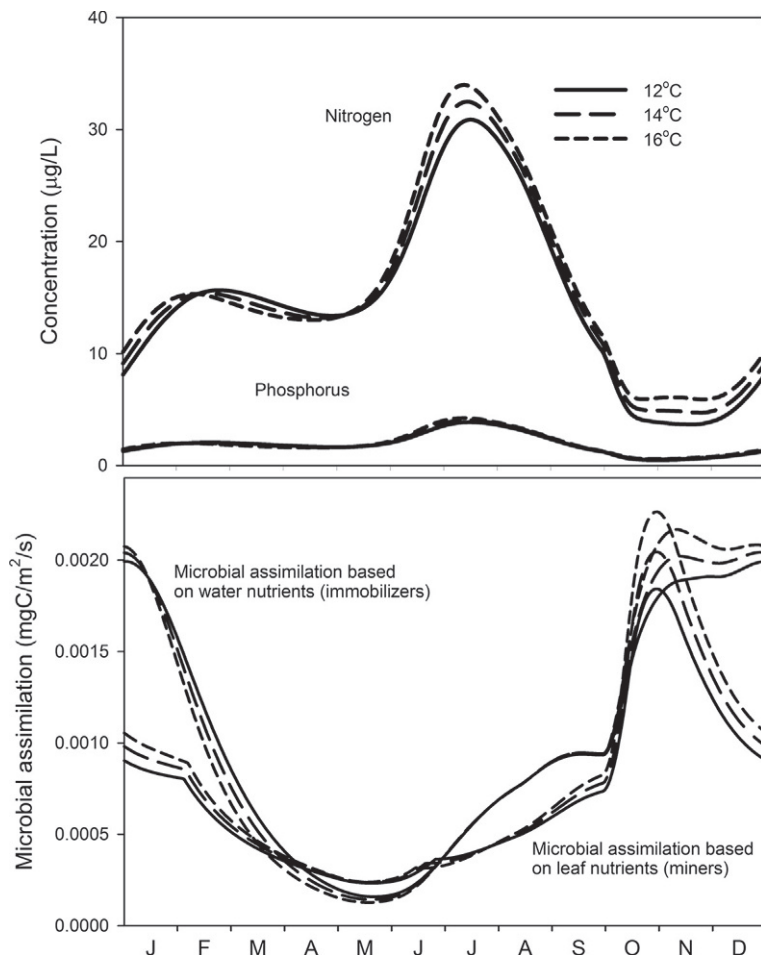


Fig. 19 Results of 2°C and 4°C temperature increases on nitrogen and phosphorus concentrations (*upper panel*) and microbial assimilation (*lower panel*). These results are from simulations of the model with both autochthonous and allochthonous inputs.

Response to Elevated Dissolved Nutrients

We saw very little response to elevated nitrogen (Table 2 and Fig. 20) by either autotrophs or heterotrophs. With higher N input and no effect on in-stream processes, dissolved N concentrations simply increased in the stream (Fig. 20), and net uptake of N (as % of input) decreased. However, there was a small increase in net uptake of P (Table 2). Because the N:P ratio of input

dissolved nutrient was slightly above the Redfield ratio (Table 3), the stream was not nitrogen limited, except briefly after autumn leaf fall; however, algae did respond to higher N by storing more N as evidenced by higher N:P ratios (Fig. 21 and Table 3). Seston exported from the stream reach was richer in N with respect to both C (Table 2) and P (Table 3).

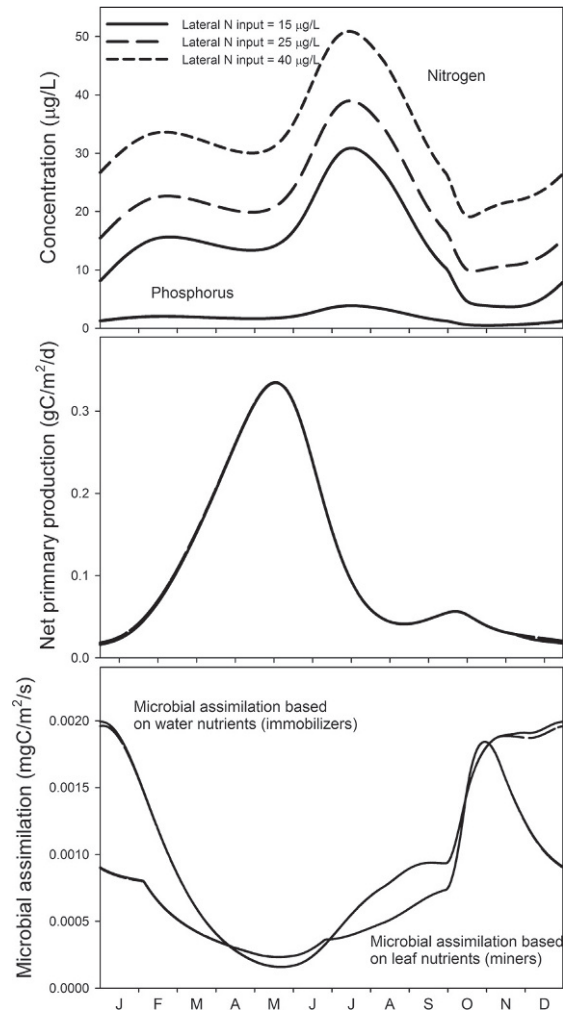


Fig. 20 Results of elevated lateral nitrogen input on nitrogen and phosphorus concentrations (*upper panel*), net primary production (*middle panel*), and microbial assimilation (*lower panel*). These results are from simulations of the model with both autochthonous and allochthonous inputs. Except for N concentration, most of the elevated N simulation lines are hidden behind the default simulation lines.

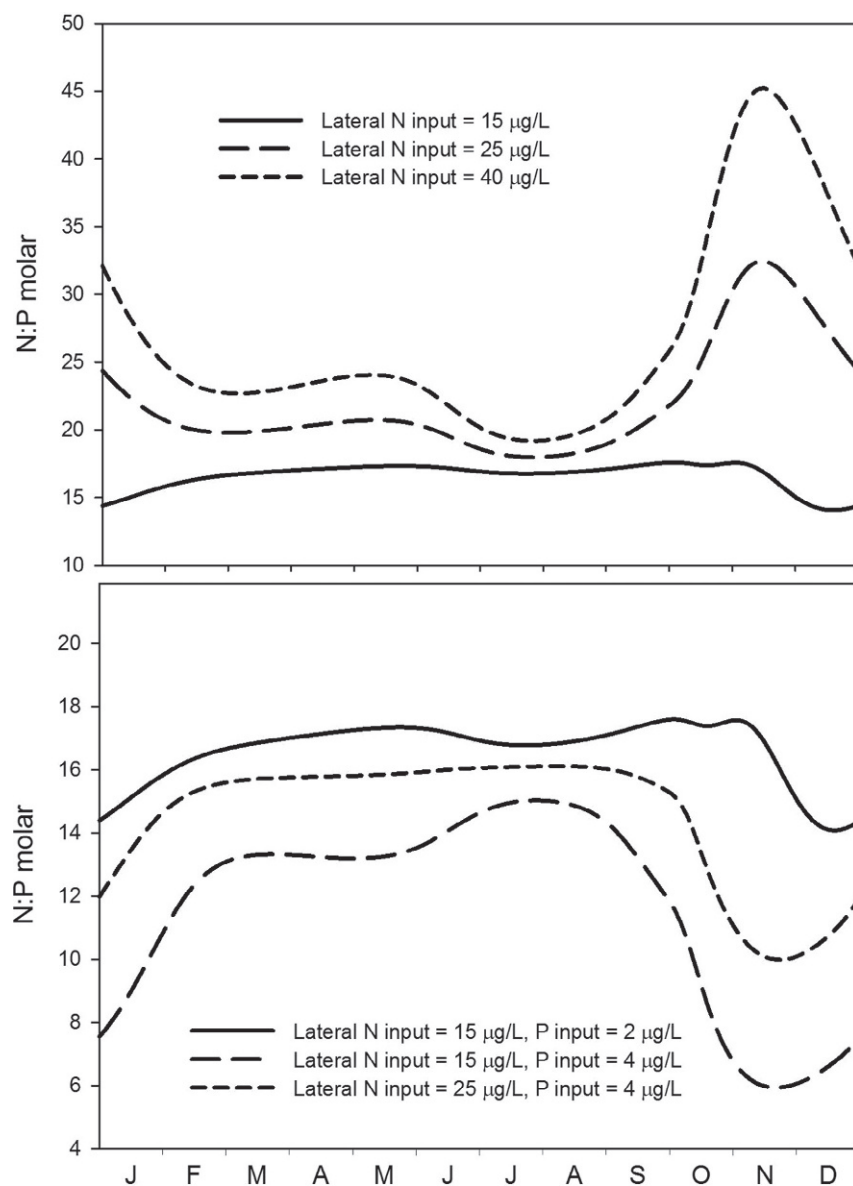


Fig. 21 Response of algal N:P ratio to elevated lateral nitrogen input (*upper panel*) and elevated lateral phosphorus input and combined elevated nitrogen and phosphorus input (*lower panel*). These results are from simulations of the model with both autochthonous and allochthonous inputs.

Similarly, with elevated P, algae stored more P (Fig. 21). The higher input of P did cause some increase in NPP in spring, though NPP was slightly lower than the default simulation in winter, so that annual NPP was changed very little (Fig. 22 and Table 2). Elevated P caused significant increase in

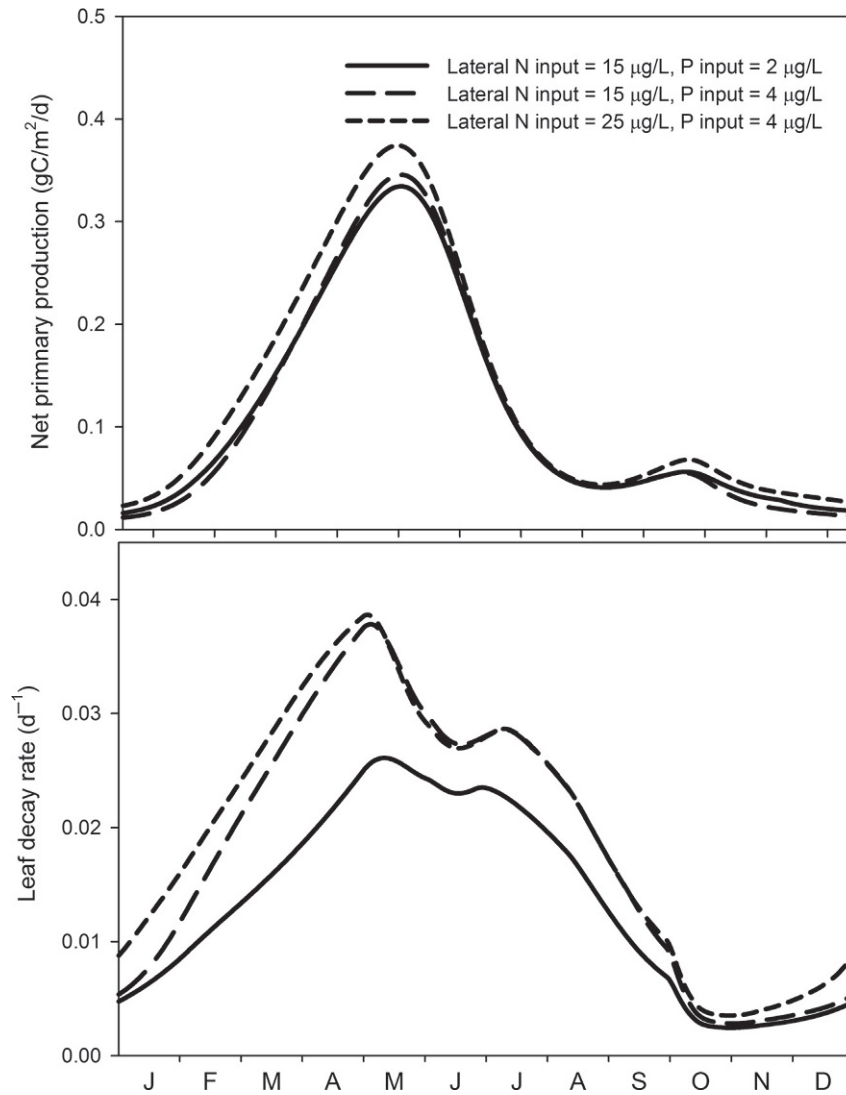


Fig. 22 Response of net primary production (*upper panel*) and leaf decay rate (*lower panel*) to elevated lateral phosphorus input and combined elevated nitrogen and phosphorus input. These results are from simulations of the model with both autochthonous and allochthonous inputs.

leaf decay rate, particularly in spring when immobilizers were the major contributors to decomposition (Figs. 22 and 23). The enhanced microbial uptake reduced dissolved N concentration in autumn and winter (Fig. 23), which accounted for the decrease in NPP at this time. Annual immobilizer

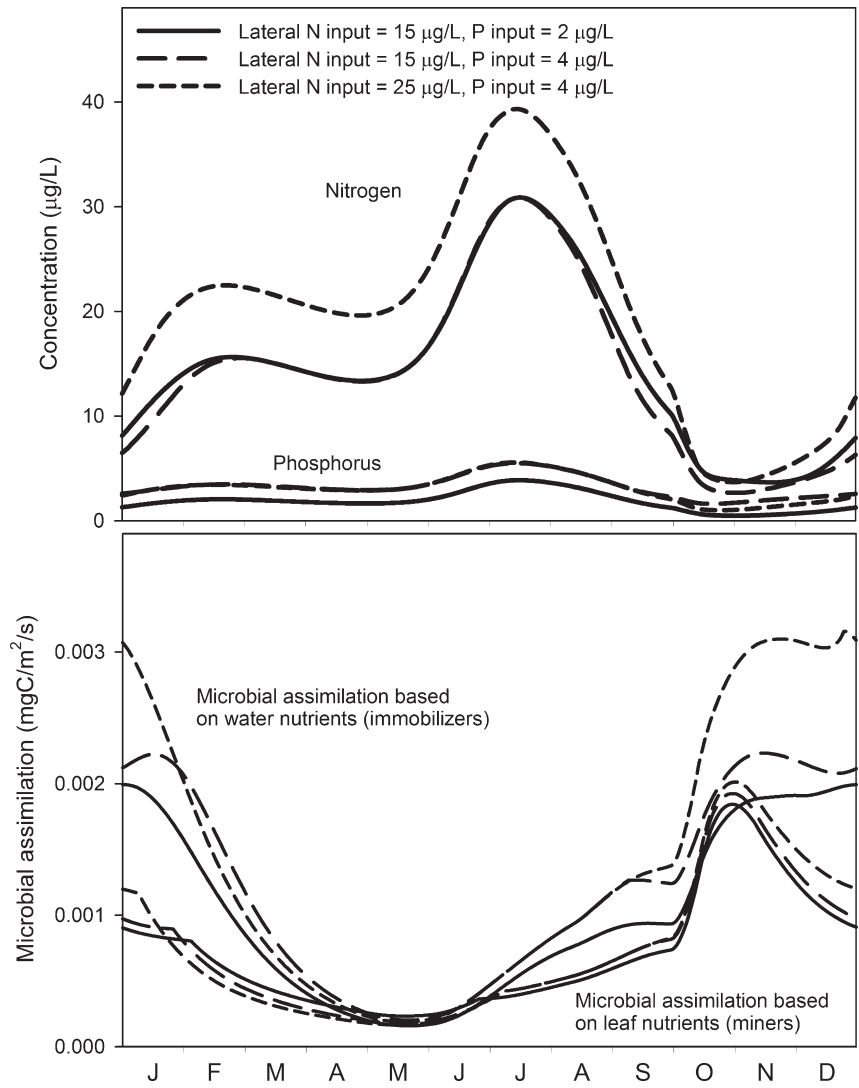


Fig. 23 Response of nitrogen and phosphorus concentrations (*upper panel*) and microbial assimilation (*lower panel*) to elevated lateral phosphorus input and combined elevated nitrogen and phosphorus input. These results are from simulations of the model with both autochthonous and allochthonous inputs.

assimilation was significantly increased, but miners were very little affected by the dissolved P increase (Fig. 23 and Table 2). As with N, the increase in P reduced net uptake of P (as % of input), but because of the elevated decay by immobilizers, net uptake of N increased (Table 2). P concentration in the water was approximately doubled through most of the year, and N was slightly reduced during the time of greatest microbial uptake (Fig. 23).

The dual N and P limitation of autotrophs was illustrated when inputs of both nutrients were elevated—NPP increased by about 15% (Fig. 22 and Table 2). Microbial immobilizer assimilation increased even more, but most of the increase can be attributed to the increase in P. The response of immobilizers to the increase in both N and P was mixed. Immobilizer assimilation was elevated from Oct. to mid-Feb., but then it was lower than with just elevated P in spring (Fig. 23). As with miner assimilation, immobilizer assimilation apparently became limited by the small amount of remaining leaf material by this time. With the addition of both nutrients, net uptake of both N and P was lower than the default simulation (Table 2). Water column concentrations of both N and P were generally elevated (Fig. 23).

CONCLUSIONS

No model is ever “correct,” but the simplifications that are necessary in the construction of models are often effective at pointing out the limitations of our knowledge. Many of the results of our simulations can probably be attributed to the parameters and inputs we used (eg, dissolved N:P ratio just above the Redfield ratio), but many of our simulation results are useful for suggesting directions for future studies.

A number of authors have called for opening the black box of microbial processes in ecosystems (eg, Tiedje et al., 1999; Schimel and Weintraub, 2003). While modern tools allow us to recognize the many kinds of microbial organisms involved in leaf decomposition, ecologists are just beginning to understand their mechanistic role in decomposition and nutrient processes. Fungi and bacteria may be synergistic (Bengtsson, 1992), and it is well-recognized that different heterotrophic microbes complement each other by the production of various enzymes that act on different components of vascular plant detritus (eg, Moorhead and Sinsabaugh, 2006; Rinkes et al., 2011). Fungi and bacteria may also function antagonistically in the decomposition of vascular plant tissue (eg, Mille-Lindblom and Tranvik, 2003). Similarly, there may be functional differentiation of microbes based on the ways they acquire and use nutrients. We know that

leaf-decomposing microbes in soil (eg, [Manzoni and Porporato, 2007](#)) and streams (eg, [Güsewell and Gessner, 2009](#); [Cheever et al., 2013](#)) use nutrients from both leaves and water, but we do not know if these processes are performed by different organisms. In our model, we have treated these as different organisms. Using this model structure, our simulations suggest that miners and immobilizers may stimulate each other through nutrient generation, and that the presence of both nutrient acquisition mechanisms increases the efficiency of leaf litter decay.

We need more mechanistic understanding of the microbial processes linking leaf decay and nutrient dynamics. We modeled uptake and use of leaf nutrients as if they are two separate processes, performed by two different kinds of microbes, immobilizers and miners, with characteristics similar to bacteria and fungi, respectively. In fact, there are perhaps thousands of kinds of microbes associated with decaying leaves in streams. Many may have enzymes both to mine nutrients from leaves and to take up nutrients from water.

The interactions of autotrophs and heterotrophic microbes have been studied primarily in planktonic systems, where both synergistic and competitive interactions have been demonstrated (eg, [Mills et al., 2008](#)). Bacterio-plankton generally rely on extracellular organic carbon excretion by algae (eg, [Gurung et al., 1999](#)), but [Bratbak and Thingstad \(1985\)](#) pointed out the paradox that algal excretion of organic carbon is used by bacteria, but these bacteria then require additional nutrients in order to use this carbon. This causes competition for nutrients, and under nutrient stress, the algae excrete more organic carbon. Bacterio-plankton have generally been shown to be better competitors for phosphorus at low concentrations (eg, [Currie and Kalff, 1984](#)), but, ultimately, bacteria cannot outcompete algae, because the algae are their only carbon source ([Mindl et al., 2005](#)). [Danger et al. \(2007\)](#) found that the bacteria-algae interaction could be competitive, communalistic, or mutualistic, depending on the relative levels of nitrogen and phosphorus.

In streams, algae may stimulate leaf decomposition by providing a more nutritious substrate for shredder leaf consumption or by stimulating bacteria and fungi by the production of exudates (eg, [Franken et al., 2005](#)). [Rier et al. \(2007\)](#) suggested that algal effects on leaf decomposition may be through stimulation of extracellular enzymes, and [Danger et al. \(2013\)](#) attributed the effect to priming, whereby labile carbon exudates increase the mineralization of more refractory leaf tissue. In our model, algal-microbial interactions are only mediated by competition for nutrients or by production

of nutrients through mineralization, which includes cellular exudates. We found that algae and microbes often competed for critical nutrients—NPP was generally higher when leaves were not present, and leaf decay was faster when there was no algal production (Fig. 17). However, we also found evidence for some synergistic interaction—during parts of the year, NPP was almost entirely based on leaf-derived nutrients, and through much of the warmer part of the year, leaf decay was faster because of nutrients originally taken up by autotrophs (Fig. 17). Thus our model captures most of the experimentally observed interactions but suggests a highly dynamic interaction where these interactions can be very different in different seasons.

Most small streams are dominated by either autochthonous or allochthonous energy input (eg, [Hagen et al., 2010](#)). Where trees shade a stream, they provide allochthonous energy but also shade the stream, limiting autochthonous production. In streams where allochthonous and autochthonous production are similar (partial riparian forest but open over the stream), interactions between autotrophs and heterotrophs can affect the retention of inorganic nutrients. Comprehensive studies of both autotrophic and heterotrophic processes have rarely been made in a single stream.

Like our stream model, many streams apparently exist very near dual nutrient limitation ([Francoeur, 2001](#); [Tank and Dodds, 2003](#)). In our simulations, the addition of a single nutrient only slightly altered metabolic activity although the algae exhibited “luxury consumption,” taking up some of the added nutrient with a consequent effect on N:P ratios. The small stimulation of metabolism, however, slightly increased the net uptake of the other nutrient (Table 2). When we added both nutrients, there was a significant increase in NPP and leaf decay, as well as in nutrient uptake. However, light and carbon (leaf detritus) limitation prevented the stream from retaining and transforming all of the additional nutrients.

Our model and that of [Webster et al. \(2009\)](#) suggest that a fairly large fraction of leaf detritus is dead microbial tissue. Our values seem high, but there are few data for comparison. Measurements of chitin and ergosterol in detritus suggest that there are relatively large amounts of living and dead fungal tissue in detritus ([Ekblad et al., 1998](#); Webster and others, unpublished data). If this material is relatively rich in N and P, it may store significant nutrients in streams, as has been suggested for forest soils ([Aber and Melillo, 2001](#); [Lindahl et al., 2002](#)). Chitin, the structural material of fungal cell walls, is especially refractory and may store significant N.

Our model has only two nutrients, which we call nitrogen and phosphorus. In the model, they differ only in the stoichiometry of their inputs

and biological processes. In fact, nitrogen and phosphorus and other important chemicals are very different, physically, chemically, and biologically (eg, Bosatta and Ågren, 1991; Hall et al., 2013). In the oxidized conditions of most streams, nitrogen occurs primarily as nitrate. Ammonium produced by biological mineralization of organic matter is rapidly nitrified. Nitrate is highly soluble and mobile. In contrast, phosphorus is highly insoluble. Under the same oxidizing conditions, phosphorus complexes with elements such as iron, combines with often-abundant divalent ions, such as calcium, and often exist at concentrations below the level of detection. Understanding and effectively modeling these differences is a challenge for stream ecologists. Nitrate may be removed from streams via denitrification, which we did not attempt to simulate in our model. Denitrification is typically much smaller than assimilatory N uptake (Arango et al., 2008; Mulholland et al., 2008), but may be similar to net N uptake. In a stream similar to our model stream, denitrification might remove ~ 1 gN/m²/year (Mulholland et al., 2009), which is far less than the average assimilatory N uptake (U) of 21.4 gN/m²/year of our combined (autotrophic-heterotrophic) simulation but similar to the annual net uptake ($U - R$) of 1.6 gN/m²/year.

Our attempt to look at possible climate change responses was limited to independent increases in temperature or nutrients. In fact, potential climate change effects on streams are very complex, including both direct and indirect effects (Davis et al., 2013). Because of the strong land-water linkages of streams, indirect effects through changes to terrestrial vegetation will likely be most critical. As pointed out by Davis et al. (2013), these terrestrially-channeled, climate change effects include such things as fire, plant species range changes, insect outbreaks, and landslides. A more complete analysis of potential climate change effects on streams would need to include both the direct and these indirect effects and their interactions.

As we pointed out previously and as noted by others (eg, Brookshire et al., 2009), streams can “retain” nutrients only temporarily. Forest ecosystems may retain nutrients by the long-term accumulation of nutrients in tree biomass or in the aggradation of soil organic matter with complexed nutrients (eg, Vitousek and Reiners, 1975). In contrast, streams alternately retain and release nutrients over far shorter periods, governed by seasonality and episodic storm exports, with relatively little year-to-year change and essentially steady-state behavior at the decadal time scale (Meyer and Likens, 1979). The within-year cycles of retention and release may produce large effects on concentration. In our combined (heterotroph-autotroph) simulations, nutrient concentrations declined through fall and winter when

heterotrophic uptake was the strongest, remained low through spring when autotrophic uptake was most active, then peaked in summer as mineralization from declining algal and microbial stocks exceeded uptake (Fig. 24). Storage and release alone, however, produces only temporal variations with no effect on long-run concentrations. Long-term effects arise from either lateral import/export (eg, nitrogen fixation or denitrification) or transformation of the form of the transported nutrient. In our combined simulation, the annual net uptake of inorganic inputs (26% of the N and 28% of the P) was exported from the reach as seston. For budgeting based only on inorganic concentrations, this transformation would have appeared as retention.

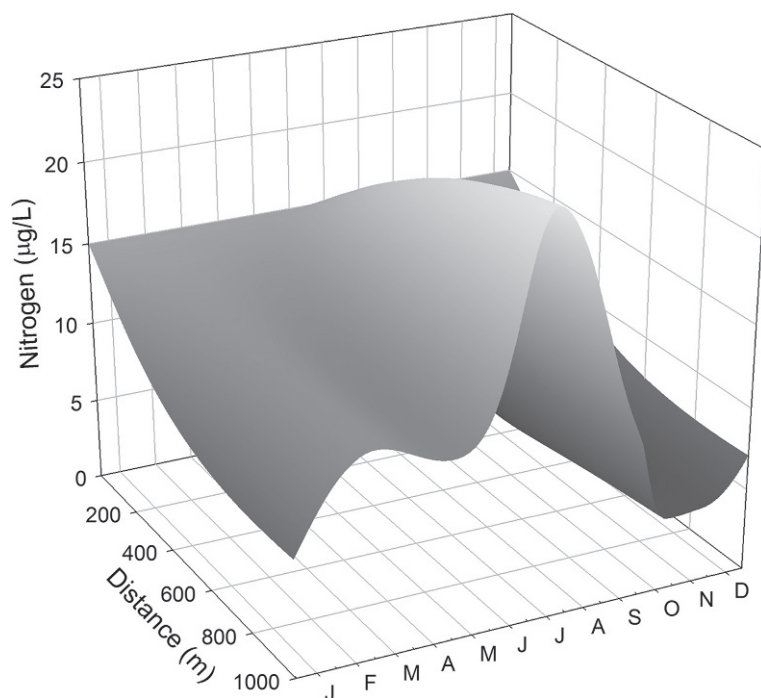


Fig. 24 Downstream and seasonal trends in nitrogen concentration in stream water from a simulations with both autochthonous and allochthonous inputs. A graph of phosphorus concentration would be qualitatively very similar.

While many studies have observed net uptake of inorganic nutrient (eg Meyer and Likens, 1979; Rigler, 1979; Doyle et al., 2003; Mulholland, 2004; Niyogi et al., 2010; Bernal et al., 2012) few have had the temporal span and coverage of nutrient forms needed to distinguish transient retention from transformation to organic exports. One study that fully succeeded in this

regard (Meyer and Likens, 1979) found that Bear Brook, New Hampshire, was in long-term steady state and that, over a 13-year period, 30% of the dissolved P inputs were transformed into particulate export. This is close to our net uptake of 28% for P, but unlike our idealized simulations, most of the particulate export from Bear Brook occurred during storms. The technical difficulties associated with measuring storm fluxes helps explain why long-term, whole-reach, complete nutrient budgets are so rare.

Both autotrophic and heterotrophic process in natural streams release dissolved organic N and P (Mulholland et al., 1988; Peterson et al., 2001; Ashkenas et al., 2004) in addition to particulates (seston) (Newbold et al., 1983; Peterson et al., 2001; Ashkenas et al., 2004; Hall et al., 2009). Both seston and dissolved organic nutrient consist of a mix of labile and more refractory forms (Ittekkot, 1988; Mulholland et al., 1988; Brookshire et al., 2005; Richardson et al., 2013). The refractory materials likely travel long distances downstream prior to mineralization (Cushing et al., 1993; Webster et al., 1999; Newbold et al., 2005). Inclusion of dissolved organic carbon and more refractory forms of seston in our model would have increased the turnover length and, correspondingly, the downstream flux of organic nutrients. Net uptake would have been greater and inorganic concentrations would have been further reduced. The potential influence of production of less labile organic matter is perhaps even greater for downstream waters such as lakes and estuaries, where the bioavailability of nutrients may be critical to algal growth (Seitzinger and Sanders, 1997; Seitzinger et al., 2002). Understanding the production, biological use, and transport, of these dissolved and particulate organic materials is a critical next step in understanding nutrient spiraling in streams.

Finally, most natural streams are not lightless tunnels through dense forests, nor are they open ditches with thick mats of algae. With the exceptions of glacial melt streams in Antarctica and urban gutters, most streams have some input of vascular plant material. And just a small forest opening will allow some algae or moss to grow, even in an iconic River Continuum (Vannote et al., 1980) headwater stream. These processes can significantly alter dissolved inorganic nutrient concentrations. Watershed budget studies that view the stream as a simple integrator of terrestrial outputs may over or underestimate the actual outputs from the landscape. Seasonal signals that originate in the stream may be incorrectly attributed to terrestrial processes. In order to quantify effectively terrestrial and stream processes, we need measurements made at springs, seeps, and the interface between groundwater and streams. Golladay et al. (1992) found significant differences in

the chemistry of stream water and samples taken from springs and near-stream lysimeters. But there have been few similar measurements (Sudduth et al., 2013). Coupled with limited measurement of dissolved organic and particulate nutrient transport (especially during storms), we still have limited ability to identify sites of nutrient transformation within watersheds. What is the relative importance of upland soils and vegetation, near-stream areas, and the streams themselves? Our results suggest that what happens in streams cannot be ignored.

DISCUSSION QUESTIONS

1. What happens to the net uptake of nutrients in streams? Is it exported primarily in dissolved organic or particulate form? In the case of nitrogen, is a significant fraction lost to denitrification? How do these processes vary among streams in different biomes?
2. Are the processes we described as mining and immobilization characteristic of specific microbial groups? Can these processes be demonstrated using mono-specific cultures of stream microbes?
3. Is it possible to experimentally demonstrate competition or synergism between miners and immobilizers in streams? Or between heterotrophs and autotrophs?
4. Would our understanding of stream nutrient uptake be improved if we had better estimates of the direct inputs of nutrients to streams (ie, springs and groundwater)?
5. How important are the indirect effects of climate change, such as changes to terrestrial vegetation, to stream processes?
6. Is it possible to measure the storage of nutrients in dead microbial tissue?
7. Why do nutrient concentrations in streams tend to reach a downstream longitudinal equilibrium (Fig. 24)?
8. What considerations should govern the level of mechanistic detail in an ecosystem model?
9. If increasing atmospheric CO₂ produces greater forest biomass accumulation and hence, greater litterfall, possibly with higher C:N ratios, how might this affect stream nutrient concentrations?

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