

Nutrient Recycling Affects Autotroph and Ecosystem Stoichiometry

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ABSTRACT: Stoichiometric nutrient ratios are the consequence of myriad interacting processes, both biotic and abiotic. Theoretical explanations for autotroph stoichiometry have focused on species' nutrient requirements but have not addressed the role of nutrient availability in determining autotroph stoichiometry. Remineralization of organic N and P supplies a significant fraction of inorganic N and P to autotrophs, making nutrient recycling a potentially important process influencing autotroph stoichiometry. To quantitatively investigate the relationship between available N and P, autotroph N : P, and nutrient recycling, we analyze a stoichiometrically explicit model of autotroph growth, incorporating Michaelis-Menten-Monod nutrient uptake kinetics, Droop growth, and Liebig's law of the minimum. If autotroph growth is limited by a single nutrient, increased recycling of the limiting nutrient pushes autotrophs toward colimitation and alters both autotroph and environmental stoichiometry. We derive a steady state relationship between input stoichiometry, autotroph N : P, and the stoichiometry of organic losses that allows us to estimate the relative recycling of N to P within an ecosystem. We then estimate relative N and P recycling for a marine, an aquatic, and two terrestrial ecosystems. Preferential P recycling, in conjunction with greater relative P retention at the organismal and ecosystem levels, presents a strong case for the importance of P to biomass production across ecosystems.

Keywords: stoichiometry, nutrient, recycling, nitrogen, phosphorus, model.

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Stoichiometric ratios of carbon to nitrogen to phosphorus (C : N : P) are often surprisingly constant within ecosystems and allow different levels of ecological organization to be easily linked. Half a century ago, Redfield (1958) described the now canonical C : N : P ratios of 106 : 16 : 1 and 105 : 15 : 1 for phytoplankton and seawater and argued that biological processes were responsible for the strikingly similar values. Over the past 2 decades, extensive sampling in the Atlantic and Pacific oceans has shown that surface C : N : P ratios vary somewhat seasonally but that deep water C : N : P ratios are remarkably constant (Karl et al. 2001; Colman et al. 2005). McGroddy et al. (2004) compiled C : N : P values for foliage and litter from terrestrial ecosystems throughout the globe and found that while C : N : P ratios vary significantly across biomes, they are constrained within a particular biome. The relative constancy of C : N : P ratios within terrestrial biomes and throughout the world's oceans suggests that a high degree of nutrient regulation occurs within ecosystems. Biotic processes that are responsible for the majority of the C, N, and P fluxes worldwide all have particular stoichiometric requirements and outputs, both of which influence organism stoichiometry and depend on the stoichiometry of the environment (Elser 2006). Because the dynamics of these elements are intimately tied to the composition of life on earth, it should be possible to relate the stoichiometry of individual organisms to ratios of C : N : P occurring at broad spatiotemporal scales.

The recycling (or remineralization; we use the terms interchangeably) of essential nutrients such as N and P from unavailable forms (most organic molecules) to available forms (inorganic and some organic molecules) is one mechanism known to exert influence on nutrient dynamics in ecosystems (Rodin and Basilevich 1967; Jordan et al. 1972; Harrison et al. 1983; Lehman 1984; Olsen et al. 1986; Azam 1998; Elser and Urabe 1999). Empirical observations of ecosystem-level nutrient dynamics indicate that the recycling of organically bound N and P is responsible for a sizable fraction of the N and P available to autotrophs. For example, in the Middle Atlantic Bight, 50%–80% of summer N production is regenerated or re-

cycled (Harrison et al. 1983). The short turnover time for the entire P pool in the euphotic zone of the oceans (on the order of weeks) points to remineralization as the key process for supplying P to phytoplankton (Colman et al. 2005). Nutrient budgets for the Hubbard Brook Experimental Forest suggest that more than 80% of N (Bormann et al. 1977) and 60% of P (Yanai 1992) uptake are supplied by recycling.

Although decades of empirical observations have shown that nutrient recycling substantially influences ecosystem nutrient dynamics, theoretical studies have not explored the full range of potential recycling effects. Early theoretical studies highlighted the importance of nutrient recycling to the stability of mineral cycles and ecosystems (Jordan et al. 1972; DeAngelis 1980; Harrison and Fekete 1980) but did not consider the dynamics of coupled elements. In more recent studies focusing on coupled N and P, Daufresne and Loreau (2001) and Grover (2002, 2004) concluded that nutrient recycling mediated by herbivory can affect nutrient limitation status and competitive outcomes between species. Daufresne and Hedin (2005) added nutrient recycling to a chemostat-type model in which autotrophs have fixed stoichiometry, and they showed that differential recycling of two essential nutrients can alter the spectrum of supply points that lead to coexistence or competitive exclusion. It is clear from these studies that nutrient recycling can qualitatively affect interspecific interactions and ecosystem stability, but it is not clear how nutrient recycling and species-specific nutrient requirements interact to influence whole ecosystem stoichiometry.

To understand the stoichiometry of both organisms and their environments, it is necessary to consider the effects of nutrient inputs, losses, and recycling simultaneously at the ecosystem level. Here, we take an initial step toward quantifying the effects of nutrient recycling on whole ecosystem stoichiometry. Using a generalized autotroph growth model, we first determine the effects of nutrient recycling on (1) organism N:P ratios, (2) inorganic N:P ratios, and (3) the relationship between organism stoichiometry and environmental stoichiometry. From a steady state relationship relating the stoichiometry of inputs and losses and autotroph stoichiometry, we estimate the degree of N recycling relative to P. We then compare the model steady state and recycling estimate with empirical data from aquatic and terrestrial ecosystems. Our model captures the effects of nutrient recycling on ecosystem-level stoichiometry and offers an alternative method for calculating the relative proportions of N and P recycled in ecosystems. Because measuring remineralization rates empirically is notoriously difficult, our model estimate, which is based on relatively accurate empirical measurements, is potentially quite useful.

A Model of Autotroph Growth with Nutrient Recycling

We extended the autotroph growth model proposed by Legovic and Cruzado (1997), which incorporates saturating resource uptake (Michaelis-Menten-Monod functional form), saturating growth as a function of internal resource stores (Droop functional form), and Liebig's law of the minimum. Models incorporating such nutrient dynamics have been used to study plant competition (Tilman 1980; Daufresne and Hedin 2005), phytoplankton growth and stoichiometry in chemostat experiments (Klausmeier et al. 2004b), and the optimal stoichiometry of marine phytoplankton (Klausmeier et al. 2004a). We eliminated the chemostat-type dynamics by decoupling inorganic nutrient inputs and losses and, following Daufresne and Hedin (2005), allowed some fraction of organic losses to be reintroduced into the inorganic nutrient pool. These changes result in the following system of equations for i essential nutrients:

$$\dot{R}_i = I_i + \epsilon_i m Q_i B - l_i R_i - f_i(R_i) B, \quad (1)$$

$$\dot{Q}_i = f_i(R_i) - \mu \text{MIN} \left[1 - \frac{Q_{\min,i}}{Q_i} \right] Q_i, \quad (2)$$

$$\dot{B} = \left\{ \mu \text{MIN} \left[1 - \frac{Q_{\min,i}}{Q_i} \right] - m \right\} B, \quad (3)$$

with nutrient uptake described by $f_i(R_i) = (v_i R_i)/(K_i + R_i)$. Inorganic resource concentration of nutrient i in the environment is R_i , autotroph resource concentration (quota) is Q_i , the minimum quota is $Q_{\min,i}$, and autotroph biomass is B . Nutrient input rates are denoted by I_i , maximum uptake rates by v_i , half-saturation constants for uptake by K_i , inorganic loss by l_i , maximum growth rate by μ , organic loss/mortality by m , and fraction of nutrient remineralized by ϵ . The minimum function (MIN) is evaluated for all i essential nutrients. Because we are ultimately interested in the dynamics of two resources, N and P, we analyze the model for two essential resources.

Model Analysis

Equilibrium

Equilibrium solutions are readily found and similar to those obtained in other studies (Legovic and Cruzado 1997; Grover 2002; Klausmeier et al. 2004b), so we simply list nontrivial equilibrium values for all state variables, some implicit in others for brevity. For two nutrients under single-nutrient limitation ("lim" for the limiting nutrient and "non" for the nonlimiting nutrient),

$$\hat{Q}_{\text{lim}} = \frac{Q_{\text{minlim}}}{1 - m/\mu}, \quad (4)$$

$$\hat{R}_{\text{lim}} = \frac{\mu m K_{\text{lim}} Q_{\text{minlim}}}{\nu_{\text{lim}}(\mu - m) - \mu m Q_{\text{minlim}}}, \quad (5)$$

$$\hat{Q}_{\text{non}} = \frac{\nu_{\text{non}} \hat{R}_{\text{non}}}{m K_{\text{non}} + \hat{R}_{\text{non}}}, \quad (6)$$

$$\hat{R}_{\text{non}} = \frac{1}{2I_{\text{non}}} \left\{ (I_{\text{non}} - l_{\text{non}} K_{\text{non}}) - \nu_{\text{non}} \Lambda \hat{B}^* + \sqrt{[(I_{\text{non}} - l_{\text{non}} K_{\text{non}}) - \nu_{\text{non}} \Lambda \hat{B}^*]^2 + 4I_{\text{non}} l_{\text{non}} K_{\text{non}}} \right\}, \quad (7)$$

$$\hat{B} = \frac{I_{\text{lim}} - l_{\text{lim}} \hat{Q}_{\text{lim}}}{(1 - \epsilon_{\text{lim}}) m \hat{Q}_{\text{lim}}}, \quad (8)$$

where $\Lambda = (1 - \epsilon_{\text{non}})/(1 - \epsilon_{\text{lim}})$ describes the ratio of proportional organic nutrient losses and $\hat{B}^* = (1 - \epsilon_{\text{lim}})\hat{B}$, which is the equilibrium biomass in the absence of nutrient recycling. Equilibrium biomass (eq. [8]) can be calculated using steady state values for either of the two nutrients. This equilibrium is locally stable when it exists and is positive, which is the only case of biological interest (see appendix). However, determining whether the equilibrium is globally stable remains an open question.

Colimitation occurs when both Droop functions in equation (3) are equal, which leads to

$$\frac{Q_{\text{min1}}}{Q_{\text{min2}}} = \frac{\hat{Q}_1}{\hat{Q}_2}. \quad (9)$$

Single-nutrient limitation occurs if the equilibrium quota of one of the nutrients increases, rendering the other limiting, and

$$\frac{Q_{\text{minlim}}}{Q_{\text{minnon}}} > \frac{\hat{Q}_{\text{lim}}}{\hat{Q}_{\text{non}}}. \quad (10)$$

Simple versus Differential Recycling

Recycling has no effect on the inorganic resource concentration or the quota of the limiting resource but can affect both the inorganic concentration and quota of the non-limiting resource and therefore the stoichiometry of both the environment and the autotrophs. This fact is easily seen by noting that the fraction of organic losses remineralized (ϵ_i) is absent from equations (4) and (5), indicating that recycling has no effect on equilibrium values. Similarly, if both the limiting and nonlimiting resources are remineralized at the same rate ($\epsilon_{\text{lim}} = \epsilon_{\text{non}}$), the organic loss ratio (Λ) disappears from equations (6) and (7) and recycling does not alter autotroph stoichiometry. However,

increasing the rate of remineralization does increase the standing stock biomass of the autotrophs, which can be seen by the influence of ϵ_i in equation (8).

If nutrients are remineralized at different rates ($\epsilon_{\text{lim}} \neq \epsilon_{\text{non}}$), then the organic loss ratio (Λ) will influence both the inorganic concentration and the quota of the nonlimiting nutrient and, consequently, the stoichiometry of both nutrient pools. We note that fractional organic losses always occur as a ratio in the equilibrium expressions for the quotas and inorganic resource pools, which is why we made the substitution $\Lambda = (1 - \epsilon_{\text{non}})/(1 - \epsilon_{\text{lim}})$. Increasing the fraction of the limiting resource recycled relative to the fraction of the nonlimiting resource recycled increases Λ and therefore decreases the concentration of both the available nutrient and the cell quota of the nonlimiting resource (see appendix). Increased recycling of the limiting resource relative to the nonlimiting resource allows more biomass to accumulate, thus drawing the concentration of the nonlimiting resource down even further.

A relative increase in the recycling of the limiting resource drives the autotrophs toward colimitation. Reducing the value of \hat{Q}_{non} by increasing Λ increases the quota ratio on the right side of the inequality in equation (10) but does not affect \hat{Q}_{lim} . We can explicitly determine the value of Λ that results in colimitation as a function of the physiological characteristics of autotrophs and environmental inputs and losses. Assuming that equation (9) holds, we can eliminate \hat{B} by setting the equilibrium biomass equations for each of the two resources (eq. [8]) equal,

$$\frac{I_1 - l_1 \hat{R}_1}{(1 - \epsilon_1) m \hat{Q}_1} = \frac{I_2 - l_2 \hat{R}_2}{(1 - \epsilon_2) m \hat{Q}_2}, \quad (11)$$

and then substituting the resource equations for both nutrients (eq. [5]) to define

$$\Lambda_{\text{colim}} \equiv \frac{I_1/Q_{\text{min1}} - l_1 \mu m K_1 / [\nu_1(\mu - m) - \mu m Q_{\text{min1}}]}{I_2/Q_{\text{min2}} - l_2 \mu m K_2 / [\nu_2(\mu - m) - \mu m Q_{\text{min2}}]}. \quad (12)$$

Whole System Stoichiometry

Often absent from studies focusing on organismal stoichiometry, especially theoretical studies, is a description of the relationship between organismal stoichiometry and environmental stoichiometry. Because organismal and environmental stoichiometry are intimately linked, both must be considered when evaluating the likelihood of a particular mechanism or set of mechanisms responsible for structuring nutrient dynamics. We can rearrange equa-

Table 1: Components of the steady state ecosystem stoichiometry equation, $\Lambda\mathcal{M} = \mathcal{R}$

Name	Equation	Value	Interpretation
Input matching ratio (\mathcal{M})	$\frac{\hat{Q}_N/\hat{Q}_P}{I_N/I_P}$	>1	Autotroph N : P greater than input N : P
		<1	Autotroph N : P less than input N : P
Inorganic retention ratio (\mathcal{R})	$\frac{1 - l_N\hat{R}_N/I_N}{1 - l_P\hat{R}_P/I_P}$	>1	Greater inorganic N retention than inorganic P retention
		<1	Greater inorganic P retention than inorganic N retention
Organic loss ratio (Λ)	$\frac{1 - \epsilon_N}{1 - \epsilon_P}$	>1	Proportion of organic P recycled greater than proportion of organic N recycled
		<1	Proportion of organic N recycled greater than proportion of organic P recycled

tion (11), replacing the numeric subscripts with N and P, to arrive at an equation that relates the stoichiometry of the inorganic available pool to the stoichiometry of nutrient inputs and recycling. This equation makes use of the organic loss ratio Λ (for N and P, $\Lambda = (1 - \epsilon_N)/(1 - \epsilon_P)$) as well as a new term \mathcal{M} , hereafter known as the input matching ratio, that expresses autotroph N : P stoichiometry as a scalar multiple of input stoichiometry ($\hat{Q}_N/\hat{Q}_P = \mathcal{M}(I_N/I_P)$):

$$\Lambda\mathcal{M}\frac{I_N}{I_P} = \frac{I_N - l_N\hat{R}_N}{I_P - l_P\hat{R}_P}. \quad (13)$$

Next, we divide both sides of equation (13) by I_N/I_P , noting that l_iR_i/I_i is the ratio of loss to input of nutrient i in the inorganic state, to arrive at

$$\Lambda\mathcal{M} = \frac{1 - l_N\hat{R}_N/I_N}{1 - l_P\hat{R}_P/I_P}. \quad (14)$$

This equation is useful because (1) it and the quantities comprising it are dimensionless and (2) the quantities comprising it—input and loss rates and organismal stoichiometry—have been measured repeatedly for a variety of ecosystems. For brevity, we refer to the right-hand side of equation (14) as the inorganic retention ratio (\mathcal{R}).

The three components of the ecosystem stoichiometry equation (14) allow us to draw inferences about ecosystem-level nutrient dynamics. For example, the input matching ratio (\mathcal{M}) indicates which nutrient needs to be recycled more for autotroph stoichiometry to match input stoichiometry. If $\mathcal{M} > 1$, autotroph N : P is greater than input N : P, whereas if $\mathcal{M} < 1$, autotroph N : P is less than input N : P. The inorganic retention ratio (\mathcal{R}) reflects the relative retention of inorganic N to inorganic P for the entire ecosystem. Values of $\mathcal{R} > 1$ indicate an increased ecosystem-level retention of inorganic N inputs relative to inorganic P inputs, with the inverse true if $\mathcal{R} < 1$. This can be seen by realizing that if $\mathcal{R} > 1$, $l_N\hat{R}_N/I_N < l_P\hat{R}_P/I_P$,

meaning that inorganic N losses relative to inputs are smaller than those for P. Finally, the organic loss ratio (Λ) is the ratio of fractional organic N loss to fractional organic P loss. Because $\Lambda = (1 - \epsilon_N)/(1 - \epsilon_P)$, if $\Lambda > 1$, the proportion of organic P recycled is greater than the proportion of organic N recycled ($\epsilon_P > \epsilon_N$). If $\Lambda < 1$, the proportion of organic N recycled is greater than the proportion of organic P recycled ($\epsilon_P < \epsilon_N$). In the absence of nutrient recycling, $\Lambda = 1$ and \mathcal{R} reflects the disparity between input stoichiometry and autotroph stoichiometry (\mathcal{M}). See table 1 for a summary of the interpretation of quantities in equation (14).

Comparison of the Model to Empirical Data

Data Sources

Using data from the literature, we examined how N and P are recycled in different ecosystems, in light of our model results. We used data from comprehensively studied aquatic (a New Hampshire lake and the North Pacific Ocean) and terrestrial (forests in Hawaii and New Hampshire) ecosystems. This compilation is by no means exhaustive but rather illustrates how our model can be used in conjunction with data to estimate the relative magnitude of elusive ecosystem processes. Because the model is sufficiently general, we were able to compare the estimated importance of N and P recycling for varied ecosystems.

Aquatic data were taken from a study of nutrient inputs to the North Pacific Gyre (Martin and Gordon 1988) and a comprehensive ecosystem study of Mirror Lake, located in New Hampshire (Likens 1985a). For the North Pacific Gyre, we pooled estimates of nutrient input resulting from diffusion, advection, and atmospheric deposition in the case of N because our model has only one inorganic nutrient input parameter. As is typical with oceanographic studies of nutrient flux, inorganic losses were not reported. Inorganic losses from the euphotic zone are rarely, if ever, reported in the oceanographic literature because they are almost impossible to measure and immaterial if net flux

Table 2: Data sources used to calculate quantities in our model

Flux/pool	Hawaii sources	Hubbard Brook sources
I_N	Crews et al. 2000; Carrillo et al. 2002; Matzek and Vitousek 2003	Bormann et al. 1977; Roskoski 1980
I_P	Chadwick et al. 1999; Carrillo et al. 2002; Vitousek 2004	Yanai 1992; Likens and Bormann 1995
\hat{R}_N	Hedin et al. 2003; Vitousek 2004	Bormann et al. 1977
\hat{R}_P	Crews et al. 1995; Hedin et al. 2003; Vitousek 2004	Yanai 1992
\hat{Q}_N	Vitousek et al. 1995; Vitousek 2004	Whittaker et al. 1979
\hat{Q}_P	Vitousek et al. 1995; Vitousek 2004	Yanai 1992
$m\hat{Q}_N\hat{B}$	Herbert and Fownes 1999	Bormann et al. 1977
Litter/(litter + root fall)	Vitousek 2004	Likens and Bormann 1995
$m\hat{Q}_P\hat{B}$	Herbert and Fownes 1999	Likens and Bormann 1995
$I_N\hat{R}_N$	Hedin et al. 2003	Bormann et al. 1977
Leaching + trace gas	Vitousek 2004	Likens and Bormann 1995; Groffman et al. 2006
$I_N\hat{R}_P$	Hedin et al. 2003; Vitousek 2004	Likens and Bormann 1995
$(1 - \epsilon_N)m\hat{Q}_N\hat{B}$	Hedin et al. 2003; Vitousek 2004	Fitzhugh et al. 2001
$(1 - \epsilon_P)m\hat{Q}_P\hat{B}$	Hedin et al. 2003; Vitousek 2004	Likens and Bormann 1995

is the only quantity of interest. Furthermore, nutrient losses from the euphotic zone occur almost entirely through export of organic matter. For Mirror Lake, inputs of both inorganic N and P result from precipitation and runoff, and losses occur through seepage and outlet flow (Likens et al. 1985). We used the average values calculated from annual input-output measurements from 1970 until 1976. Likens (1985*b*) calculated phytoplankton \hat{Q}_N/\hat{Q}_P to be 15.5 : 1, which is the value we used to calculate the input matching ratio (\mathcal{M}) from I_N/I_P .

The terrestrial forest ecosystem data are from a long-term chronosequence of montane tropical rainforests on the Hawaiian Islands (for a summary, see Vitousek 2004) and the Hubbard Brook Experimental Forest in the White Mountains of New Hampshire (for a summary, see Likens and Bormann 1995). The Hawaiian sites progress from N limited at the young sites to P limited at the old sites (Vitousek and Farrington 1997). We estimated the organic loss ratio (Λ) from forest data in up to three ways, each of which assumes steady state of the relevant pools. The first two methods estimate each ϵ_i independently and use them to calculate Λ . First, we recognized that $1 - \epsilon_i$ is the fraction of litter fall lost as organic losses and used data from organic losses (lysimeters and/or streams) and litter fall (Λ^{\dagger}). Second, we used the inorganic pool to estimate mineralization rates, with atmospheric deposition, fixation or weathering (where relevant), and mineralization as inputs and plant uptake and inorganic leaching (and trace gas loss for N) as losses (Λ^{\ddagger}). From this mineralization rate, we estimated ϵ as in the first case. Finally, we estimated Λ from equation (14) using the data for inorganic inputs, losses, and organismal stoichiometry ($\hat{\Lambda}$). Note that the plant N and P quotas are calculated from sun foliage

for the Hawaiian sites but from both sun foliage and total aboveground biomass for Hubbard Brook. Also note that N and P fluxes from plant to soil are litter fall only for the Hawaiian sites but are litter fall and litter fall plus root fall for Hubbard Brook. Finally, organic P losses are dissolved organic P in the Hawaiian sites and particulate organic P in Hubbard Brook. Table 2 lists the sources used to compute the terrestrial entries in table 3.

Using the Model to Interpret Empirical Observations

A striking feature of the data in table 3 is the apparent importance of P across ecosystems. The input matching ratio (\mathcal{M}) is derived using reliable empirical measurements and indicates that, with the exception of the North Pacific Gyre, autotrophs are supplied with relatively sufficient N but insufficient P. The decrease in \mathcal{M} observed for the Hawaiian chronosequence, indicating increased need to retain P over time, is driven primarily by changes in nutrient inputs because plant N : P is virtually constant through time (Vitousek 2004). As can be seen in table 3, N inputs remain remarkably similar through time, but P inputs decrease significantly. If the input matching ratio (\mathcal{M}) is <1 , indicating that autotroph N : P is less than input N : P, we might intuitively expect increased ecosystem-level P retention relative to N ($\mathcal{R} < 1$). Empirical values of the inorganic retention ratio (\mathcal{R}) are <1 for terrestrial forests, meaning that a greater proportion of P inputs compared with N inputs are retained. The slightly inconsistent values for the youngest Hawaiian forest ($\mathcal{R} > 1$ and $\mathcal{M} < 1$) are not extreme enough to warrant much attention because the value of 1.08 for the inorganic retention ratio (\mathcal{R}) could easily be the result of measure-

Table 3: Measured values and estimates from equation (14) for inorganic N and P (IN, IP) inputs and losses, \mathcal{R} , \mathcal{M} , and Λ

Ecosystem	Input		Loss		\hat{Q}_N/\hat{Q}_P	\mathcal{R}	\mathcal{M}	$\hat{\Lambda}$	Λ^\dagger	Λ^\ddagger
	IP	IN	IP	IN						
North Pacific Gyre	34.1	478	NA	NA	16	≈ 1	1.14	.88	NA	NA
Mirror Lake	.2	33.4	.14	13.6	15.5	1.99	.09	21.9	NA	NA
Hubbard Brook watershed ^a	1.33	135	.06	90.6	13.5	.34	.13	2.69	.87	NA
Hubbard Brook watershed ^b	1.33	135	.06	90.6	28.2	.34	.28	1.21	33.0	NA
Hawaiian forests (age):										
300 years	5.53	217	.59	7.66	32.4	1.08	.83	1.31	3.98	.72
20,000 years	2.11	142	.14	109	31.1	.25	.46	.54	3.57	.27
150,000 years	.71	152	.12	74.0	22.6	.62	.11	5.57	8.14	2.85
1,400,000 years	.18	153	.12	130	27.4	.72	.03	19.9	5.51	.54
4,100,000 years	.13	140	.20	166	31.2	.46	.03	NA	8.25	12.5

Note: $\hat{\Lambda}$ is estimated from \mathcal{R} and \mathcal{M} using equation (14). Λ^\dagger is estimated from the organic loop. Λ^\ddagger is estimated from the inorganic loop. Input and loss units are $\mu\text{mol day}^{-1}$. Boldface values indicate a violation of the steady state assumption. For \mathcal{R} , ecosystem-level losses of both inorganic N and P are greater than inorganic inputs. For Λ^\ddagger , the proportion of inorganic N and P recycled is >1 for both nutrients. NA = not applicable.

^a Total biomass N : P and stream losses are used to calculate \mathcal{M} and Λ^\ddagger .

^b Foliar N : P and lysimeter losses are used to calculate \mathcal{M} and Λ^\ddagger .

ment error. Any measurement error is further magnified by the fact that measurements are presented in a ratio. However, the inconsistent values of $\mathcal{R} = 1.99$ and $\mathcal{M} = 0.091$ for Mirror Lake are worthy of note and are discussed below. The value of 0.46 for the oldest Hawaiian forest is in boldface because losses are greater than inputs for both inorganic N and P, which is incompatible with the steady state assumption. Potential causes are discussed below.

The relative efficiency of nutrient recycling occurring in an ecosystem is the third indicator of nutrient utilization we derived from the ecosystem stoichiometry equation. The organic loss ratio (Λ), which reflects relative proportions of N and P recycled in an ecosystem, is different from the input matching ratio (\mathcal{M}) and the inorganic retention ratio (\mathcal{R}) because it is a function of quantities, ϵ_N and ϵ_P , that are extremely difficult to measure empirically. The ecosystem stoichiometry equation is useful because it allows the organic loss ratio (Λ) to be estimated using only \mathcal{R} and \mathcal{M} , both of which are based on reliable measurements. The ability to estimate Λ with relative confidence from empirical data is appealing because calculating Λ using more direct measurements of nutrient remineralization yields variable and conflicting results.

The organic loss ratio (Λ) is highly sensitive to the method used for its calculation. The approach we introduce here, which relies on steady state model solutions, simply divides \mathcal{R} by \mathcal{M} to obtain $\hat{\Lambda}$. If nutrient inputs, losses, and stoichiometry of autotrophs in an ecosystem are accurately measured, and if our model is a reasonable representation of nutrient dynamics, the model-based estimate $\hat{\Lambda}$ should be relatively reliable. To maintain steady state stoichiometry in response to decreasing P inputs that

intensify P limitation in Hawaii, the relative proportion of P recycled must increase with forest age because both plant N : P and ecosystem-level nutrient retention remain relatively constant (Matzek and Vitousek 2003; Vitousek 2004). The organic loss ratio calculated from the ecosystem stoichiometry equation ($\hat{\Lambda}$) increases as expected with increasing P limitation over time (table 3). We did not calculate $\hat{\Lambda}$ for the oldest Hawaiian forest because losses of both inorganic N and P are greater than inputs at this site, violating the steady state assumption needed to use this approach. The organic loss ratio can also be estimated directly from empirical measurements associated with either the organic or inorganic loop, as described above (we restrict our comparison to the Hawaiian forests because calculation of Λ on the basis of both the organic and inorganic loop is not possible, given the data available for the other ecosystems). As indicated in table 3, Λ^\dagger (estimated from the organic loop) appears to be a more reliable indicator of nutrient recycling than Λ^\ddagger (estimated from the inorganic loop). In addition to being qualitatively consistent with the expectation of $\Lambda > 1$ because of the relative ease of breaking down organic P compared with organic N (Vitousek and Howarth 1991), Λ^\dagger tends to increase with forest age, as did $\hat{\Lambda}$, in line with expectations (Vitousek 2004). In contrast, the Λ^\ddagger values observed are <1 , indicative of greater relative N recycling, in all but one case, which seems unlikely given the greater ecosystem-level P retention ($\mathcal{R} < 1$) and greater organism-level P retention ($\mathcal{M} < 1$) consistent with P limitation. Furthermore, Λ^\ddagger does not increase through time as expected with increasing P limitation. In fact, ϵ_N and ϵ_P used to calculate Λ^\ddagger for the oldest Hawaiian forest are both >1 , indicating that more

than 100% of one nutrient is recycled, which is impossible given the steady state assumption.

The disparity in the organic loss ratio values for Hubbard Brook further underscores the sensitivity of this quantity to empirical measurements used for its calculation. The values for the first Hubbard Brook line in table 3 are calculated using total biomass N : P and stream dissolved organic nitrogen (DON) loss, whereas the alternate values are based on foliar N : P and lysimeter measurements. The $\hat{\Lambda}$ values estimated from the ecosystem stoichiometry equation are consistent with greater relative P retention for both sets of measurements. The input matching ratio \mathcal{M} for total biomass is less than the input matching ratio for foliage because of the increased N content in leaves, but both values qualitatively indicate a greater need for P retention relative to N. The organic loss ratio $\hat{\Lambda}$ for total biomass is greater than the organic loss ratio for foliage, as is necessary to maintain the model equilibrium. The most significant difference between the two measurements of nutrient loss is observed in Λ^\ddagger . Stream dissolved organic (DO) losses suggest slightly preferential N retention, whereas lysimeter DO losses suggest strong preferential P retention. On the basis of the inorganic retention ratio \mathcal{R} and the input matching ratio \mathcal{M} , we expect Hubbard Brook to retain more P but not so much that $\Lambda^\ddagger = 33.0$. This expectation is based on both the knowledge of the Hubbard Brook ecosystem (Likens and Bormann 1995) and the data for the Hawaiian chronosequence. The values of \mathcal{R} and \mathcal{M} for Hubbard Brook place it between the 20,000-year-old and the 150,000-year-old Hawaiian forests, but the Λ^\ddagger value >30 for Hubbard Brook is at odds with the values ranging from 3 to 8 for Hawaii.

Discussion

In this article, we have quantified the effects of simple nutrient recycling on equilibrium stoichiometry of autotrophs and their environments. We incorporated the remineralization of N and P into a model of autotroph growth in which autotrophs have flexible stoichiometry. The addition of nutrient recycling affects stoichiometry only if nutrients are differentially remineralized. As recycling of the limiting nutrient increases, effectively increasing its supply rate, autotrophs draw down the concentration of the nonlimiting nutrient, which pushes them toward colimitation. We derived a simple steady state relationship linking input and loss stoichiometry to the stoichiometry of autotrophs and available nutrients, which enabled us to estimate the relative N and P recycling for terrestrial and aquatic ecosystems using reliable empirical measurements. Recycling estimates along with empirical descriptions of nutrient retention suggest that P often plays a more influential role than N in limiting autotroph

growth. This is certainly not the first theoretical study to include and assess the effects of nutrient recycling on autotroph growth dynamics. But, to our knowledge, it is the first to examine the relationship between differential nutrient recycling and whole system stoichiometry for a range of ecosystems. Our approach differs from previous modeling studies that incorporate nutrient recycling since we did not study the effects of recycling on interspecific interactions. We instead chose to study how autotrophs as a functional group interact with their environments to determine the stoichiometry of major nutrient pools.

An important result of this analysis, absent from previous theoretical studies that incorporate nutrient recycling, is the elucidation of the steady state relationship between nutrient inputs and losses, nutrient recycling, autotroph stoichiometry, and stoichiometry of inorganic nutrients. Earlier studies examining the effects of recycling on ecosystems focused on isolated nutrients at the ecosystem level (Jordan et al. 1972; DeAngelis 1980; Harrison and Fekete 1980), not stoichiometry. It is necessary to consider inorganic nutrient pools and recycling because autotrophs utilize inorganic N and P and recycling is the process by which the majority of inorganic N and P are supplied (Bormann et al. 1977; Harrison et al. 1983; Yanai 1992). In addition to relating nutrient pools and fluxes in a transparent and general manner, the ecosystem stoichiometry equation (eq. [14]) facilitates across ecosystem comparisons because it is dimensionless and therefore unaffected by the choice of units used to quantify nutrient pools and fluxes or the size of ecosystems being compared. It is appropriate for describing the steady state stoichiometry of any ecosystem consisting of autotrophs and their resources. The degree to which autotroph N : P departs from input N : P, indicated by the input matching ratio (\mathcal{M}), is inversely related to the organic loss ratio (Λ), meaning that if autotroph N : P decreases relative to input N : P, a greater relative proportion of P than N must be recycled to maintain the same value for the inorganic retention ratio (\mathcal{R}). Here we have considered a generic autotroph pool, but in multispecies ecosystems, autotroph N : P is determined by the relative abundance of all autotroph species, meaning that autotroph N : P and \mathcal{M} may vary because of interspecific competition (Daufresne and Hedin 2005; Schade et al. 2005).

Ecosystem ecologists have long known that recycling contributes substantially to available inorganic nutrient pools (Jordan et al. 1972), but the difficulty associated with making direct measurements has prevented its widespread quantification. The ecosystem stoichiometry equation (14) is particularly useful because it provides an estimate of the relative recycling of N to P and can be used to evaluate empirical measurements of remineralization. Furthermore, it is still useful in the absence of detailed

information describing autotroph nutrient uptake and growth. Although the exact values of the quantities in the ecosystem stoichiometry equation are determined by specific physiological mechanisms in our model, the equation links autotroph stoichiometry, input stoichiometry, and loss stoichiometry in a general manner. At face value, the ecosystem stoichiometry equation simply relates steady state concentrations of nutrients and fluxes, which is why we were able to calculate Λ for multiple ecosystems without knowledge of autotroph physiology. However, specifying particular functions for growth and nutrient uptake yields a deeper understanding of how recycling affects the stoichiometry of different nutrient pools in ecosystems.

The generality of the ecosystem stoichiometry equation allowed us to calculate organic loss ratios (Λ), which indicate the degree of N recycling relative to P, for multiple aquatic and terrestrial ecosystems using only inorganic nutrient inputs, losses, and autotroph stoichiometry. Overall, estimated values are consistent with hypothesized nutrient limitation in the ecosystems considered and the more relevant of the two direct recycling estimates, Λ^{\dagger} . Calculating Λ from the organic loop is natural given our interest in organic nutrient dynamics, and Λ^{\dagger} agrees with both inorganic retention ratio (\mathcal{R}) and input matching (\mathcal{M}) qualitatively and quantitatively much better than $\hat{\Lambda}^{\ddagger}$, calculated from the inorganic loop. The ratios Λ^{\dagger} and $\hat{\Lambda}$ are always >1 for terrestrial ecosystems, which makes sense given the biochemistry of P (mostly connected via ester bonds, which are easily clipped by extracellular phosphatases) versus that of N (which forms many more recalcitrant bonds; Vitousek and Howarth 1991). Furthermore, both tend to increase with forest age in Hawaii, which is expected since P becomes more limiting through time. The ratio Λ^{\ddagger} , estimated from the inorganic loop, fluctuates above and below 1 with no consistent pattern through the chronosequence, and the value for the oldest Hawaiian forest is illogical given the definition of the organic loss ratio and the steady state assumption. An organic loss ratio of <1 for the North Pacific Gyre supports the idea that the Gyre has, for the recent past, been N limited (Karl et al. 2001), although this estimate is based on the assumption of approximately equal ecosystem-level retention of N and P. Because the high organic loss ratio (Λ) for Mirror Lake (consistent with the hypothesized P limitation in temperate lakes [Schindler 1974]) may initially appear to be at odds with an inorganic retention ratio (\mathcal{R}) >1 (indicative of greater biological utilization and retention of N versus P relative to inputs), we discuss the potentially counterintuitive values in detail below. Finally, the qualitative disparity between Λ^{\dagger} values for Hubbard Brook demonstrates how different measurements can significantly alter the conclusions we might draw about nutrient dynamics.

The three estimates of the organic loss ratio (Λ) are

based on different assumptions and empirical measurements, all of which come with caveats. The difficulty associated with measuring gaseous N losses directly affects our estimate of ecosystem-level nutrient utilization, as described by the inorganic retention ratio \mathcal{R} , and in turn affects our model-based estimate of the organic loss ratio Λ (as well as the direct empirical estimate of Λ calculated using the inorganic loop). The P inputs are often hard to quantify, especially in old terrestrial ecosystems, and measurement error will significantly affect calculations of the organic loss ratio using the organic or inorganic loop. Calculations based on the inorganic loop are further confounded by the fact that direct measurements of N uptake can result in $\epsilon_N > 1$, which is illogical given our model formulation. Using different types of organic nutrient loss to calculate the organic loss ratio from the organic loop yields qualitatively different values of Λ^{\dagger} . Stream DON losses lead us to believe that relative N recycling is marginally greater than relative P recycling, whereas lysimeter DON losses suggest that relative P recycling is of much larger magnitude than relative N recycling.

Although we have related the stoichiometry of multiple nutrient pools in a simple ecosystem, we did not include the nutrient dynamics associated with organisms at higher trophic positions. Omitting the nutrient dynamics associated with higher trophic levels is more of a problem in ecosystems that are not dominated by primary producers, such as Mirror Lake, in which a significant proportion of the total biomass resides higher in the food web (Likens 1985a). For Mirror Lake, the value for the inorganic retention ratio ($\mathcal{R} = 1.99$) indicates that a greater proportion of inorganic N inputs are taken up and retained relative to the proportion of inorganic P inputs retained, which would seem to indicate a biological preference for N over P. However, the very low value of the input matching ratio ($\mathcal{M} = 0.09$) indicates that phytoplankton contain significantly more P relative to N than what is available to them from inorganic inputs alone. In an ecosystem consisting of only phytoplankton and their physical environment, greater proportional inorganic P losses would seem to be at odds with excess inorganic N inputs. The steady state described by the ecosystem stoichiometry equation ($\Lambda\mathcal{M} = \mathcal{R}$) reconciles the potentially counterintuitive values of the inorganic retention ratio (\mathcal{R}) and the input matching ratio (\mathcal{M}) through high proportional recycling of organically bound P relative to the proportional recycling of organically bound N ($\Lambda = 21.9$). Greater recycling of organic P relative to organic N posited by our model may reflect realistic remineralization by microbial communities but may also reflect the exclusion of important nutrient pools and fluxes in our model. Consumers, which we do not include, exert significant control over the excretion of organically bound nutrients by con-

centrating elements consumed in excess in feces and by sequestering less available elements in biomass (Darchambeau et al. 2005). As a consequence, the consumer-driven nutrient recycling (Sterner and Elser 2002) observed in more trophically complex food webs could potentially be responsible for the high organic N losses relative to P ($\Lambda > 1$) required to maintain the model steady state. If consumer N : P is less than phytoplankton N : P, consumers excrete both inorganic and organic N, which can account for excess available N for uptake by phytoplankton as well as high organic N losses relative to P. When appropriate, future studies aiming to determine the causes of large-scale stoichiometric patterns should explicitly incorporate all relevant ecosystem components.

The particular formulation we used to describe the uptake of available nutrients in large part determines the steady state solutions of the model and is more well suited to certain autotrophs than others. Nutrient uptake follows the popular Michaelis-Menten-Monod form, and as a result, autotrophs independently draw concentrations of essential nutrients down to levels specified by physiological parameters. For example, nutrient uptake of a nonlimiting resource is independent of an autotroph's internal concentration of that nutrient. Furthermore, there is no interaction between the uptake of different resources. As a consequence, nutrient uptake by autotrophs for which some degree of substitutability in resources exists will not be well characterized by the uptake kinetics we used. Additionally, homeostatic organisms that are able to regulate nutrient uptake based on internal concentrations require some modification of the uptake formulation used here. As noted earlier, however, the ecosystem stoichiometry equation (14) does not depend on nutrient uptake kinetics, only on steady state nutrient concentrations, rendering it quite useful to assess the degree to which nutrients are recycled differentially across ecosystems.

Empirical observations of increased P retention relative to N, as well as preferential P recycling across ecosystems, suggest that P availability may often exert more influence on primary production than N availability. As P becomes more limiting through succession in Hawaiian forests, both the input matching ratio and the inorganic retention ratio decrease, reflecting tighter cycling of P at both the

organismal and ecosystem levels. For autotroph stoichiometry to deviate from input stoichiometry, as indicated by a deviation of the input matching ratio (\mathcal{M}) from 1, internal nutrient concentration must be regulated somehow. But, regardless of how the nutrient regulation required for \mathcal{M} to differ from 1 occurs, the fact that the input matching ratio is <1 for all ecosystems except for the North Pacific Gyre indicates that P is often preferentially retained over N at the organismal level. Further evidence for the importance of P to terrestrial ecosystems is the preferential P retention at the ecosystem level, as indicated by the inorganic retention ratio (\mathcal{R}). Preferential P recycling is a mechanism that allows P retention to increase while P inputs decrease and autotroph stoichiometry remains constant over successional time in Hawaii. The increase in nutrient recycling efficiency that occurs as ecosystems develop (Odum 1969) can result from interspecific competition that maximizes resource use intensity at both the autotroph and decomposer trophic levels (Loreau 1998). Finally, the importance of nutrient recycling in mature terrestrial ecosystems highlights an important difference from nutrient dynamics in marine environments. Primary producers are believed to drive whole ecosystem stoichiometry though fast turnover relative to mixing in the oceans (Falkowski and Davis 2004), yielding an input matching ratio of approximately 1. Because phytoplankton take up virtually all available N and P and can regulate N inputs through fixation to match their preferred stoichiometry (Tyrell 1999), N : P of water in the oceans is thought to be determined by phytoplankton stoichiometry. Therefore, the departure of the input matching ratio from 1 for terrestrial ecosystems, over succession in particular, points to an absence of Redfield-like regulation of nutrient stoichiometry on land.

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APPENDIX

Local Stability of Nontrivial Equilibrium

The Jacobian for the system limited by resource 1 and ordered $\hat{R}_1, \hat{Q}_1, \hat{B}, \hat{R}_2, \hat{Q}_2$ is

$$J = \begin{pmatrix} -l - \hat{B}f'_1(\hat{R}_1) & \epsilon_1 m \hat{B} & \epsilon_1 m \hat{Q}_1 - f_1(\hat{R}_1) & 0 & 0 \\ f'_1(\hat{R}_1) & -\mu & 0 & 0 & 0 \\ 0 & \frac{\mu \hat{B} Q_{\min 1}}{\hat{Q}_1^2} & \mu \left(1 - \frac{Q_{\min 1}}{\hat{Q}_1}\right) - m & 0 & 0 \\ 0 & 0 & \epsilon_2 m \hat{Q}_2 - f_2(\hat{R}_2) & -l - \hat{B}f'_2(\hat{R}_2) & \epsilon_2 m \hat{B} \\ 0 & \frac{-\mu Q_{\min 1} \hat{Q}_2}{\hat{Q}_1^2} & 0 & f'_2(\hat{R}_2) & -m \end{pmatrix}. \quad (\text{A1})$$

At the nontrivial equilibrium, $\mu(1 - Q_{\min 1}/Q_1) - m = 0$, implying that the (3, 3) entry in the Jacobian is 0. Notice that J can be written in terms of blocks, which results in a lower triangular matrix:

$$\begin{bmatrix} D_1 & 0 \\ L & D_2 \end{bmatrix}.$$

It is therefore necessary to determine only the eigenvalues of D_1 and D_2 . The characteristic polynomial for D_1 is

$$\lambda^3 + (\mu + l + \hat{B}f'_1(\hat{R}_1))\lambda^2 + (\mu l + \mu \hat{B}f'_1(\hat{R}_1) - \epsilon_1 m \hat{B}f'_1(\hat{R}_1))\lambda - f'_1(\hat{R}_1) \frac{\mu \hat{B} Q_{\min 1}}{\hat{Q}_1^2} (\epsilon_1 m \hat{Q}_1 - f_1(\hat{R}_1)) = 0. \quad (\text{A2})$$

In order for the eigenvalues of D_1 to have negative real parts, which guarantees local stability, the coefficients of the characteristic polynomial must satisfy the Routh-Hurwitz criteria ($a_1 > 0$, $a_3 > 0$, and $a_1 a_2 > a_3$). The first coefficient is clearly positive: $a_1 = (\mu + l + \hat{B}f'_1(\hat{R}_1)) > 0$. The second coefficient can be simplified so that

$$a_2 = \mu l + m \hat{B}f'_1(\hat{R}_1) \left(\frac{\mu}{m} - \epsilon_1 \right), \quad (\text{A3})$$

which is always positive because $\mu > m$ and $0 < \epsilon < 1$. For the third coefficient, note that at the nontrivial equilibrium, $f_1(\hat{R}_1) = m \hat{Q}_1$. Making this substitution yields

$$a_3 = \frac{\mu m \hat{B}f'_1(\hat{R}_1) Q_{\min 1} (1 - \epsilon_1)}{\hat{Q}_1}, \quad (\text{A4})$$

which is always positive because of the restricted range of ϵ . Finally, we need to show that $a_1 a_2 - a_3 > 0$. From the characteristic polynomial and equations (A3) and (A4), we obtain

$$a_1 \left[\mu l + m \hat{B}f'_1(\hat{R}_1) \left(\frac{\mu}{m} - \epsilon_1 \right) \right] - \frac{\mu m \hat{B}f'_1(\hat{R}_1) Q_{\min 1} (1 - \epsilon_1)}{\hat{Q}_1}, \quad (\text{A5})$$

which can be rewritten as

$$a_1 \mu l + m \hat{B}f'_1(\hat{R}_1) \left[a_1 \left(\frac{\mu}{m} - \epsilon_1 \right) - \frac{\mu Q_{\min 1} (1 - \epsilon_1)}{\hat{Q}_1} \right]. \quad (\text{A6})$$

By noting that

$$a_1 = \mu + l + \hat{B}f'_1(\hat{R}_1) > \mu, \quad (\text{A7})$$

$$\mu > m, \quad (\text{A8})$$

$$\hat{Q}_1 \geq Q_{\min 1}, \quad (\text{A9})$$

we see that

$$a_1 \left(\frac{\mu}{m} - \epsilon_1 \right) - \frac{\mu Q_{\min 1} (1 - \epsilon_1)}{\hat{Q}_1} > 0. \quad (\text{A10})$$

and because all other terms in equation (A3) are positive, $a_1 a_2 > a_3$, satisfying the Routh-Hurwitz criteria for a three-dimensional system (for details, see May 1973).

Because the eigenvalues of D_1 all have negative real parts, stability of the entire system is clear because $\text{trace}(D_2) < 0$ and $\det(D_2) > 0$, guaranteeing that the eigenvalues of D_2 also have negative real parts. Therefore, the nontrivial equilibrium is locally linearly stable.

The Effect of Differential Recycling on Inorganic Nutrient Concentration and Quota of the Nonlimiting Nutrient

To determine how the ratio of fractional organic losses affects both the equilibrium inorganic nutrient concentration and quota of the nonlimiting nutrient, we differentiate the expressions for both with respect to Λ . For the nonlimiting nutrient quota,

$$\frac{d\hat{Q}_{\text{non}}}{d\Lambda} = \frac{\nu_{\text{non}} K_{\text{non}}}{m(K_{\text{non}} + \hat{R}_{\text{non}})^2} \frac{d\hat{R}_{\text{non}}}{d\Lambda}, \quad (\text{A11})$$

with

$$\frac{d\hat{R}_{\text{non}}}{d\Lambda} = \frac{\nu_{\text{non}} \hat{B}^*}{2l} \left[-1 - \frac{I_{\text{non}} - l_{\text{non}} K_{\text{non}} - \nu_{\text{non}} \Lambda \hat{B}^*}{\sqrt{(I_{\text{non}} - l_{\text{non}} K_{\text{non}} - \nu_{\text{non}} \Lambda \hat{B}^*)^2 + 4l_{\text{non}} I_{\text{non}} K_{\text{non}}}} \right], \quad (\text{A12})$$

and $\hat{B}^* > 0$ because we are concerned only with cases for which $\hat{B} > 0$. First, we note that $\nu_{\text{non}} K_{\text{non}} / m(K_{\text{non}} + \hat{R}_{\text{non}})^2 > 0$. Next, we notice that because $4l_{\text{non}} I_{\text{non}} K_{\text{non}} > 0$, the fraction in brackets in equation (A12) is always < 1 , which means that $d\hat{R}_{\text{non}}/d\Lambda < 0$ and $d\hat{Q}_{\text{non}}/d\Lambda < 0$.

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