Abstract. The fate of carbon (C) in organisms, food webs, and ecosystems is to a major extent regulated by mass-balance principles and the availability of other key nutrient elements. In relative terms, nutrient limitation implies excess C, yet the fate of this C may be quite different in autotrophs and heterotrophs. For autotrophs nutrient limitation means less fixation of inorganic C or excretion of organic C, while for heterotrophs nutrient limitation means that more of ingested C will “go to waste” in the form of egestion or respiration. There is in general a mismatch between autotrophs and decomposers that have flexible but generally high C:element ratios, and consumers that have lower C:element ratios and tighter stoichiometric regulation. Thus, C-use efficiency in food webs may be governed by the element ratios in autotroph biomass and tend to increase when C:element ratios in food approach those of consumers. This tendency has a strong bearing on the sequestration of C in ecosystems, since more C will be diverted to detritus entering soils or sediments when C-use efficiency is low due to stoichiometric imbalance. There will be a strong evolutionary pressure to utilize such excess C for structural and metabolic purposes. This article explores how these basic principles may regulate C sequestration on different scales in aquatic and terrestrial ecosystems.

Key words: carbon; C sequestration; ecosystems; C-use efficiency; grazing; nitrogen; phosphorus; stoichiometry, role in carbon sequestration.

INTRODUCTION

From the classical works of Lindeman (1942) onwards, the concept of “energy flow” in food webs has been and remains a cornerstone in ecological theory in which the height of the trophic pyramid, and thus community structure of the food web, is limited by the efficiency of energy transfer between trophic levels (Hutchinson 1959, Hairston et al. 1960). The extent to which trophic structure controls trophic efficiency or vice versa is, however, not trivial. Hairston and Hairston (1993) argued that trophic structure should be the main determinant of energy transfer and trophic efficiency. They also pointed to the fact that aquatic food chains have high transfer efficiency of energy and matter compared with terrestrial food chains. A more detailed account of this has been provided by Cebrian (1999), who illustrated clearly how variation in trophic efficiency across different ecosystems was linked with autotroph growth rate and nutrient quotas, with a strong gradient from forest ecosystems at one extreme to planktonic ecosystems at the other. The high transfer efficiency of C in planktonic systems may be attributed to both high cell quotas of N and P relative to C (high-quality food for reasons given below) and to decreased importance of low-quality structural matter like lignins and cellulose that are poorly assimilated. These factors point to fundamental differences between ecosystems, not only with regard to the transfer and sequestration of carbon, but also with regard to community composition and ecosystem function in more general terms. One key determinant of these ecosystem processes is the relative abundance of key elements, i.e., “ecological stoichiometry” (Sterner and Elser 2002).

While energy is most appropriately given in terms of joules, it is more convenient to use carbon (C) as a basic currency for the overall flow of both energy and matter. First of all, C is the major element in living materials, contributing roughly 50% of dry mass. Second, C is easily measured simultaneously with other key elements in organic tissue. Third, the C cycle has per se become a theme of major interest in a “global-change” context, and to a large extent the global effects are the sum of uptake and sequestration of C in aquatic and terrestrial ecosystems. Ecological stoichiometry is a tool for analyzing how the balance of the multiple elements required by organisms affects production, nutrient cycling, and food-web dynamics (Sterner and El-
The origins of stoichiometry are rooted in agricultural studies involving Liebig’s law of the minimum. In the stoichiometric approach, ratios of C, N, and P are compared in consumers and prey and the element in shortest supply relative to demand identified (Hessen 1992). Limiting elements are expected to be utilized for growth and transferred in food chains with high efficiency, while nonlimiting elements, by definition present in excess, must be disposed of and may be recycled. The validity of this approach has been demonstrated for a wide variety of heterotrophic organisms including bacteria (Tezuka 1990, Anderson 1992), algae (Myklestad 1977, Berman-Frank and Dubinsky 1999), protozoa (Caron and Goldman 1988), and zooplankton (Elser et al. 1988, Sterner and Hessen 1994, Elser and Urabe 1999).

In its first formulation, Liebig’s law was restricted to the supply of mineral elements to plants as fertilizers, but later formulations have also attempted to include other factors such as temperature. In a pure stoichiometric context, however, it is our view that the law of the minimum should only be applied to the elements that are used as components in growth; with this use, the law of the minimum has a direct connection to more recent ideas related to the chemical stoichiometry of living biomass. Other factors that influence growth, such as temperature, do this by changing the rates at which all the elemental resources are utilized, but without necessarily altering the underlying stoichiometry (but see Woods et al. [2003]).

In its first formulation, Liebig’s law was restricted to the supply of mineral elements to plants as fertilizers, but later formulations have also attempted to include other factors such as temperature. In a pure stoichiometric context, however, it is our view that the law of the minimum should only be applied to the elements that are used as components in growth; with this use, the law of the minimum has a direct connection to more recent ideas related to the chemical stoichiometry of living biomass. Other factors that influence growth, such as temperature, do this by changing the rates at which all the elemental resources are utilized, but without necessarily altering the underlying stoichiometry (but see Woods et al. [2003]).

In its first formulation, Liebig’s law was restricted to the supply of mineral elements to plants as fertilizers, but later formulations have also attempted to include other factors such as temperature. In a pure stoichiometric context, however, it is our view that the law of the minimum should only be applied to the elements that are used as components in growth; with this use, the law of the minimum has a direct connection to more recent ideas related to the chemical stoichiometry of living biomass. Other factors that influence growth, such as temperature, do this by changing the rates at which all the elemental resources are utilized, but without necessarily altering the underlying stoichiometry (but see Woods et al. [2003]).

In its first formulation, Liebig’s law was restricted to the supply of mineral elements to plants as fertilizers, but later formulations have also attempted to include other factors such as temperature. In a pure stoichiometric context, however, it is our view that the law of the minimum should only be applied to the elements that are used as components in growth; with this use, the law of the minimum has a direct connection to more recent ideas related to the chemical stoichiometry of living biomass. Other factors that influence growth, such as temperature, do this by changing the rates at which all the elemental resources are utilized, but without necessarily altering the underlying stoichiometry (but see Woods et al. [2003]).

In its first formulation, Liebig’s law was restricted to the supply of mineral elements to plants as fertilizers, but later formulations have also attempted to include other factors such as temperature. In a pure stoichiometric context, however, it is our view that the law of the minimum should only be applied to the elements that are used as components in growth; with this use, the law of the minimum has a direct connection to more recent ideas related to the chemical stoichiometry of living biomass. Other factors that influence growth, such as temperature, do this by changing the rates at which all the elemental resources are utilized, but without necessarily altering the underlying stoichiometry (but see Woods et al. [2003]).

In its first formulation, Liebig’s law was restricted to the supply of mineral elements to plants as fertilizers, but later formulations have also attempted to include other factors such as temperature. In a pure stoichiometric context, however, it is our view that the law of the minimum should only be applied to the elements that are used as components in growth; with this use, the law of the minimum has a direct connection to more recent ideas related to the chemical stoichiometry of living biomass. Other factors that influence growth, such as temperature, do this by changing the rates at which all the elemental resources are utilized, but without necessarily altering the underlying stoichiometry (but see Woods et al. [2003]).

In its first formulation, Liebig’s law was restricted to the supply of mineral elements to plants as fertilizers, but later formulations have also attempted to include other factors such as temperature. In a pure stoichiometric context, however, it is our view that the law of the minimum should only be applied to the elements that are used as components in growth; with this use, the law of the minimum has a direct connection to more recent ideas related to the chemical stoichiometry of living biomass. Other factors that influence growth, such as temperature, do this by changing the rates at which all the elemental resources are utilized, but without necessarily altering the underlying stoichiometry (but see Woods et al. [2003]).

In its first formulation, Liebig’s law was restricted to the supply of mineral elements to plants as fertilizers, but later formulations have also attempted to include other factors such as temperature. In a pure stoichiometric context, however, it is our view that the law of the minimum should only be applied to the elements that are used as components in growth; with this use, the law of the minimum has a direct connection to more recent ideas related to the chemical stoichiometry of living biomass. Other factors that influence growth, such as temperature, do this by changing the rates at which all the elemental resources are utilized, but without necessarily altering the underlying stoichiometry (but see Woods et al. [2003]).

In its first formulation, Liebig’s law was restricted to the supply of mineral elements to plants as fertilizers, but later formulations have also attempted to include other factors such as temperature. In a pure stoichiometric context, however, it is our view that the law of the minimum should only be applied to the elements that are used as components in growth; with this use, the law of the minimum has a direct connection to more recent ideas related to the chemical stoichiometry of living biomass. Other factors that influence growth, such as temperature, do this by changing the rates at which all the elemental resources are utilized, but without necessarily altering the underlying stoichiometry (but see Woods et al. [2003]).
ent kinds of factors be called orthogonal to indicate that they can act on growth independently of each other. Nevertheless the concept of a single limiting element is open to question—the complexity of organism physiology means that there may be circumstances where co-limitation of more than one resource is possible. For example cultures of yeast can be co-limited by both oxygen and glucose supply rates (Duboc and von Stockar 1998), shifting between different degrees of aerobicity in response to the oxygen:glucose supply rate.

The concept of stoichiometric regulation is by no means restricted in application to individual organisms. The literature abounds with statements inferring elemental limitation of whole systems, such as N limitation in terrestrial and marine systems (Rastetter et al. 1991) and P limitation in freshwater systems (Schindler 1977). Human intervention in the global cycles of carbon, nitrogen, and phosphorus (Vitousek et al. 1997, Falkowski et al. 2000) is now changing the relative availability of the elements with potential global effects on climate and ecosystems. For example, accompanying the well-known alterations in atmospheric CO$_2$ due to combustion of fossil fuels, major changes in nutrient loading have also occurred in the form of combustion processes and agricultural activity that in recent decades has led to considerable increases in availability of N and P to the biosphere (Galloway et al. 1995, Vitousek et al. 1997, Falkowski et al. 2000). Thus, an understanding of the factors that couple C to nutrient fluxes to regulate the sequestration and net balance of C in ecosystems is imperative (Giardina and Ryan 2000, Grace and Rayment 2000). In this article we discuss the scaling up of stoichiometric theory for single organisms (the focus of most published work) to whole ecosystems, focusing in particular on the impact of nutrient-loading scenarios on C sequestration.

**STOICHIOMETRY OF CELLS AND ORGANISMS**

*What autotrophs do, what heterotrophs do, and what happens when the two come together*

Much has been learned by studying and identifying the consequences of systematic variations in the C:N:P stoichiometry of organisms. One key contrast is found when considering photoautotrophs (hereafter, “autotrophs”) vs. heterotrophs, especially Metazoans. While animals generally tend to maintain body elemental composition within relatively narrow bounds, autotrophs have a large flexibility in their C:nutrient ratios and these ratios vary systematically with the growth rate of the plant. Both N:C and P:C ratios increase when the relative growth rate (RGR) of an autotroph is increasing, indicating, in relative terms, a larger relative allocation to active N- and P-based compounds than C-based structural compounds (Kooijman et al. 2004, Vrede et al. 2004). This variability in stoichiometry is characteristic of the overall plasticity of autotrophic organisms and has its physiological base in the ability of autotrophs to maintain a balance between the types of compounds required for growth (Droop 1974). Another cause of variability in stoichiometry comes from excess uptake of elements, i.e., autotrophs have considerable capacity to accumulate elements in excess of what is not immediately needed for growth. The ability to take up an excess of available elements can most clearly be seen when RGRs of a terrestrial autotroph and an aquatic autotroph are plotted as a function of nutrient C ratios (Fig. 2). The terrestrial plant *Betula pendula* took up little N or P above what was required to achieve its maximum RGR, whereas one aquatic autotroph, *Dunaliella tertiolecta*, took up N to an excess of 50% and another one, *Monochrysis lutheri*, took up P to a concentration five times that required for maximum RGR. The reasons for, and the consequences of, these two sources of variability in element ratios are, of course,
entirely different and should not be confused. When comparing C:element ratios in various autotrophs, in different habitats, or in different seasons, it is therefore necessary to know whether the element in question is limiting or not.

In contrast to the great physiological plasticity in growth form, tissue allocation, and thus biochemical and elemental composition exhibited by autotrophic organisms, metazoans exhibit far less intraspecific plasticity with a relatively narrow range of interspecific variation in C:N:P ratios, and a generally nutrient-rich biomass compared with autotrophs (Andersen and Hessen 1991, Elser et al. 2000, Sterner and Elser 2002). Thus, when consumers encounter autotroph biomass with low nutrient content, constraints on animal growth imposed by limiting nutrients seem inevitable. The net effect of stoichiometrically imbalanced food on growth rate is illustrated by growth rates of *Daphnia magna* feeding on different quantities and qualities of the green alga *Selenastrum capricornutum* (Fig. 3). While there is a drop in growth rate from medium (1 mg C/L) to low (0.5 mg C/L) food levels, reflecting food-quantity effects, growth rate also declines with increasing C:P ratio for both food concentrations, illustrating how limitation by C and P may work in tandem. Given the frequency of high C:element ratios in autotrophs, herbivores in both freshwater and terrestrial food webs may suffer from such stoichiometric constraints (Elser et al. 2001). Indeed, there is now convincing field evidence for direct P limitation of growth of the aquatic herbivore *Daphnia* (Elser et al. 2000, DeMott et al. 2001) and of the terrestrial herbivore *Manduca sexta* (Perkins et al., 2004).

Thus, with increasing nutrient imbalance between autotroph biomass and consumer, there will be less C diverted up the grazing food chain. This may also in part explain the commonly poor correlations between autotroph and grazer biomass. That is, C fixed by photosynthesis does thus not yield increased biomass at higher trophic levels in any straightforward manner. This is illustrated by the relationship between phytoplankton biomass in lakes vs. the abundance of Cladocera, the main herbivorous group of freshwater plankton (Fig. 4). While some of this scatter is likely caused by grazer–algae dynamics, changes in phytoplankton community structure with increased nutrient inputs, and top-down control of cladoceran biomass (i.e., by fish predation), the correlations remain equally poor even when excluding lakes where fish predation pressure is considered high (Hessen et al. 2003).

Stoichiometric imbalance also plays a key role in affecting decomposer and detritivore guilds that encounter nutrient-poor plant detritus. Indeed, such imbalances are likely to be even more severe than in herbivory, at least in the initial stages of detrital processing, as it is common in terrestrial plants for considerable nutrients to be reclaimed from leaves and other tissues prior to loss (Killingbeck 1993). Of particular interest are the consequences of differences between fungi and bacteria in their nutrient requirements. Fungi
appear to have low N:C or P:C ratios while the heterotrophic bacteria have typically high (yet somewhat flexible) N:C and P:C ratios (Sterner and Elser 2002, Vadstein 2000), implying that fungi and bacteria may have different roles in mineralization. Such stoichiometric relations are important for maintaining ecosystem element cycles with the consequence that soils are relatively richer in N than C relative to plants. Indeed, decomposition of soil organic matter, a key process in soil ecosystem functioning (Griffiths et al. 2000), may be limited by C, N, or P depending on soil type, management, and vegetation. Stoichiometric effects likely extend into other parts of soil food webs. As for invertebrate herbivores, invertebrate decomposers have typically one order of magnitude higher N and P concentrations in their bodies than fresh plant litter (Swift et al. 1979). By processing soil organic matter with a high C:N ratio, decomposers require extra N to produce new microbial biomass. In situations in which the pool of available inorganic N is limited, the energy-conversion efficiency (yield) or the consumption rate of the microbes, and hence decomposition, will decrease (Ågren et al. 2001). A distinguishing feature of the decomposition system is that the decomposers start with a material rich in C and hence are N or P limited but, as the substrate is used, C is released and the limiting element incorporated until a critical C:element ratio is reached where C becomes limiting. The decomposers can then release N and P and make these nutrients available for uptake by plants again. These critical break points in C:N and C:P ratios are well-defined stoichiometric quantities (Ågren and Bosatta 1998). Their values, however, are coupled to inorganic-nutrient availability (Ågren et al. 2001). A consequence of the use of inorganic N and P is that organic-matter processing by decomposers may be much less constrained by the C:nutrient ratios than by herbivore linkages.

In summary, we have provided a brief overview of factors influencing organismal stoichiometry and how this bears on C processing in ecological systems. There are many ongoing studies examining nutrient limitation of autotrophs and heterotrophs, and the fate of resulting excess C. Certainly there is still much to be learned here. In particular, the Liebig-type approach to determining limiting factors is simplistic and becoming outdated. New approaches to understanding and modeling stoichiometric interactions will need to consider in greater detail the complex interplay between elements, biochemical constraints, and the physiology of organisms (Kooijman 1998, Anderson et al. 2004).

**Enrichment Scenarios and Stoichiometry of Ecosystems**

In whole ecosystems, the sequestration of C depends on nutrient inputs, the extent to which these nutrients control C flow along food chains, and the position and strengths of the C sinks within the overall flow network. Diagrams illustrating C flows and sinks in forest and open-ocean ecosystems are shown in Fig. 5. Major sinks in terrestrial systems are aboveground biomass, roots, and soils. The living biomass supported by aquatic systems is low, but C stores in freshwater sediments may be of greater importance than commonly assumed (cf. Dean and Gorham 1998). The major sinks in the open ocean are dissolved organic and inorganic C (along with burial in sediments on long time scales). Continental margins also play a major role in ocean biogeochemical cycles, as they are burial sites of organic C derived from both local production and terrestrial sources. The added complexity of whole ecosystems in comparison to individual organisms gives rise to the expectation that the stoichiometric control of overall nutrient and C cycling is likely to be similarly complex.

---

**Fig. 5.** Schematic diagram of flows of carbon in marine and terrestrial ecosystems. Major C sinks are indicated in boldface type.
Changes in C storage capacity in ecosystems can be explained in terms of three biogeochemical factors (Rastetter et al. 1992): the total supply of nutrients from external sources, the distributions of C, N, and other elements between different system components, and alterations in the stoichiometric ratios of the components themselves. In this section we describe the biogeochemical pathways leading to C sequestration in terrestrial and aquatic systems, and examine the importance of stoichiometry in determining fluxes to C sinks, using loading scenarios (topical in the context of climate change) for illustrative purposes. We propose that incorporating organism-level responses and stoichiometric mechanisms operating at key points in ecosystem flows are central in understanding these patterns.

Terrestrial systems

Vegetation and soils are major global C sinks, 640 and 1358 Gt C/yr, respectively (Cao and Woodward 1998). Many terrestrial ecosystems are considered to be N limited in the sense that added N will produce a plant growth response and increase C storage (e.g., Vitousek and Howarth 1991). Carbon sequestration depends on the distribution of C and nutrient elements between vegetation and soils, because the C:nutrient stoichiometry of vegetation and soils differs greatly (Townsend et al. 1996). Furthermore, there are tight couplings between ambient CO2 and N uptake of terrestrial vegetation because of the key role of N-rich rubisco in C fixation (see Vrede et al. 2004). Under a prevailing N limitation of terrestrial autotrophs (Gutschik 1981, Schlesinger 1991), increased deposition of N may sequester more CO2 and elevated CO2 may allow for increased uptake of N (Schindler and Bayley 1993), provided that C:N ratios remain rather constant. Modeling studies of the response of the terrestrial biosphere to elevated CO2 indicate increases in net primary productivity and also in vegetation C:N ratio (Rastetter et al. 1997). Long-term effects of CO2 on forest growth are intimately linked with the availability of N (Oren et al. 2001). Peterson and Melillo (1985) calculated that, assuming C:N ratios in vegetation and soils remain unchanged and that 60% of N in precipitation is invested in net growth, enhanced N deposition resulting from fossil-fuel combustion could lead to significantly increased storage in forest ecosystems. Similarly, Mäkinpää et al. (1999) modeled forest response to increased N deposition and predicted an 11% increase in total C stock (vegetation, litter, and soil organic matter). On the other hand, a further increase in N loadings may reduce the uptake efficiency due to combined ammonia and nitrate acidification or shift to other limiting constituents. This “N saturation” causes increased leaching of N from soils due to “saturation” effects (Aber et al. 1989, Stoddard 1994), with increased levels of NO3 in surface water.

The ability of terrestrial ecosystems to sequester C also depends on individual plant traits due to the effects of competition for light and nutrients in determining biomass allocation in plants (Tilman 1988). Nutrient deficiency enhances biomass partitioning to roots; conversely, increased nutrient supply induces decreased root: shoot ratio (Ericsson 1995, Andrews et al. 2001). The reduced water stress associated with elevated CO2 also tends to decrease root: shoot ratio, particularly in plants not subject to severe nutrient limitation (Friedlingstein et al. 1999). The combination of high C:N ratio (>300) and long lifetimes in wood (>100 years) (Vitousek et al. 1988, Schimel et al. 1994) means that any sustained decrease in root: shoot ratio could significantly increase overall storage of C and decrease nutrient retention in forest ecosystems. Moreover it is well known that the N content of leaves and other organs of plants grown under elevated CO2 are lower than in plants cultivated at ambient CO2 (Ceulemans and Mousseau 1994, Curtis 1996, Curtis and Wang 1998, Norby et al. 2001), creating potential for increased C sequestration. The extent to which the C:N ratio of woody tissues might respond to CO2 is however less clear. Most studies have only looked at effects on N and, in a compilation of results of various studies, Cotrufo et al. (1998) report a mean plant-tissue N concentration in elevated CO2 of 86% of the concentration in ambient CO2. Variability in the extent of nitrogen-content response is, however, large among studies but there are some systematic responses: nitrogen-fixing plants and C4 plants show little response in N content to altered CO2 regime. Data regarding elements other than N are too limited to allow any general conclusions. However, a study by Overdieck (1993) indicates that tissue N:P might decrease under elevated CO2 but the ratio of N to other elements remains unchanged. The extent to which the C:N ratio of woody tissues might be responsive is however less clear.

Another aspect to consider in an ecosystem context is retranslocation of elements before tissue is shed, leading to large reduction in element:C ratio in the litter produced. Although the biochemical processes involved in retranslocation might differ for N and P, there seems to be no major difference in efficiency in their retranslocation (Aerts 1996, Killingbeck 1996). Whether this pattern remains under an increasing atmospheric CO2 concentration remains to be evaluated. However, decreases in the N:C ratio of live tissue in CO2-fertilization experiments with plants do not reliably translate to similar changes in plant litter (Norby and Cotrufo 1998). Thus, consequences for turnover rates of litter as a result of a changing N:C ratio are not clear. Although it has frequently been shown that the N:C and P:C ratios reflect the decomposability of litter (e.g., Melillo et al. 1982, Enriquez et al. 1993), these ratios could also reflect the importance of differences in carbon chemistry to the decomposer community rather
than the importance of differences in stoichiometry per se (Joffre and Ågren 2001).

Elevated CO₂ also increases the direct input of organic C into the soil through plant exudation (van Veen et al. 1991, Dukes and Field 2000). The extent to which such effects will increase the mass of litter and soil C pools depends on how this extra C supply affects microbial decomposition, which is constrained by the need for microbes to maintain their C:nutrient balance (Paul and Clark 1989). For example, if an increase in the C:N ratio of soil organic matter results in N limitation of microbial populations, decomposition could slow under elevated CO₂ leading to increased mass in litter and soil C pools. When considering the impact of climate change on soil C storage it is however necessary to consider not only response to elevated CO₂, but also the simultaneous effects of temperature (Gorissen et al. 1995). Climate warming is thought to reduce soil C by increasing microbial demand for C through increased respiration (Kirschbaum 2000). If the N thereby remineralized is sequestered into aboveground woody biomass, C stored in forest ecosystems as a whole could increase (Rastetter et al. 1991). Soil C:N ratios also have strong bearings on aquatic recipients, since the export of dissolved organic C (DOC) to surface waters has a strong positive correlation with the soil C:N ratio (Aitkenhead and McDowell 2000). Ecosystem export of DOC increased linearly from <5 to ~100 kg C·ha⁻¹·yr⁻¹ over a soil C:N ratio of ~13–30 (by mass).

Aquatic systems

Inorganic C is abundant in water, and so any increase in concentration resulting from anthropogenic CO₂ emissions might be expected on first glance to have little or no impact on phytoplankton growth and subsequent food-web dynamics. Consider, for example, the "biological pump" in the ocean that transports C via sinking particles and dissolved organic matter (DOM) from the surface euphotic zone to below the permanent thermocline, where it is eventually sequestered (in either organic or inorganic form). If photosynthesis is not limited by C, then it seems that the biological pump cannot sequester anthropogenic CO₂. It should however be noted that sequestration of anthropogenic CO₂ does occur as a result of the "solubility pump," which is the uptake of C by air–sea exchange driven by under-saturation of pCO₂ with respect to the atmosphere and subsequent transport of C-enriched waters to depth by physical processes (Follows et al. 1996). Nevertheless climate change will impact the biological pump through its effect on the natural C cycle in the ocean. For example, changes in circulation as a result of warming may alter the supply of nutrients to the surface ocean as well as the light environment experienced by phytoplankton. These changes in turn affect plankton community structure and export of organic matter.

The effects of changing nutrient supply on C cycling are commonly associated with freshwater systems because of their close proximity to human activity. Most lakes are considered to be P limited, based on close correlations between total (or particulate) P and particulate C (Fig. 6) or some other measure of biomass. Adding more P (and subsequently N) leads to eutrophication; primary production will draw on CO₂ dissolved in water, hence more atmospheric CO₂ will enter the aquatic system for conversion to algal biomass, potentially sedimenting and thus being sequestered into a C sink. In fact, freshwater sediments may represent an important storage pool for organic C, recent data suggest that many lakes commonly are net conduits of CO₂ (del Giorgio and Peters 1993, Cole et al. 1994) due to allochthonous imports of organic C from their watersheds. While CO₂ fluxes to some extent are governed by the pCO₂ gradients across the water–air boundary layer, biological processes and stoichiometric balance will also be major determinants of net CO₂ balance. Freshwater systems are also prone to large variations in CO₂, and even a moderate increase in CO₂ could yield increased C:P ratios in algae (Burkhart and Riebsell 1997, Urabe et al. 2003). This effect is demonstrated in the freshwater chlorophyte Selenastrum capricornutum in Fig. 7.

Loading of organic carbon diverted into heterotrophs will increase the output of oxidized C, while increased loading of P and N will increase primary production and thus work in the opposite direction. Based on a survey of published data, del Giorgio and Peters (1993) found that the epilimnetic P:R (primary production to community respiration) ratio rises above 1 only in rarer productive lakes. Their empirically derived equations for production (P) and respiration (R) in lakes as related to algal biomass (expressed as chlorophyll a, in micrograms per liter) were: \( P = 10.3 \times \text{chl} \times 10^{1.19} \) and \( R = 59 \times \text{chl}^{0.56} \). In their model \( P \) and \( R \) reached 1 at 14 μg chlorophyll/L, below which the lakes became net sources of CO₂. Since algal biomass and chlorophyll are proxies of phosphorus concentrations, this can be recast as a rough expression of the net exchange of CO₂ or the P:R ratio as a function of the P concentration, illustrating the bearing of P load on net C sequestration (Fig. 8).

Carbon export in the ocean depends on the balance between recycling of material in surface waters and export to depth, the former dominating in most instances. Thus it is important to understand the stoichiometry of processes controlling trophic dynamics in marine systems, and in particular those closely related to the production of particles and dissolved organic matter that are exported. Much of the particulate export is in detritus, consisting of nonliving phytoplankton aggregates (“marine snow”, Lampitt et al. 1993) and zooplankton fecal pellets. This material is clearly subject
**Fig. 6.** Regressions of particulate (seston) fractions of carbon (PC), nitrogen (PN), and phosphorus (PP) based on a survey of 110 Norwegian lakes sampled four times during the ice-free season (i.e., a total of 440 samples).

**Fig. 7.** Phytoplankton C:P ratios along a CO₂ concentration gradient in ambient medium. Algal cultures (*Selenastrum capricornutum*) were cultured in flow-through chemostats at low dilution rate (280 mL/d) with buffered medium to avoid changes in pH. Different CO₂ concentration levels were produced by bubbling equilibrated industrial-grade gas through the chemostats. There were four replicates for each treatment. Data are means and 1 SD.

**Fig. 8.** Net CO₂ balance in a large number of lakes as predicted from the model of del Giorgio and Peters (1993). The dashed lines indicate the community production:respiration ratio ($P:R = 1$) and the corresponding concentration of total P (TP). For further explanation see *Enrichment scenarios...: Aquatic systems.*
to processing by heterotrophs, and therefore might be expected to have elevated C:N ratios if nutrient elements are limiting to consumers. For example, it is known that the C:N ratio of zooplankton fecal pellets is variable and sometimes high (see Anderson 1994).

The C:N ratio of dissolved organic matter (DOM) may often be significantly higher than the Redfield ratio (e.g., Søndergaard et al. 2000). DOM in aquatic systems is produced via various processes such as phytoplankton exudation, zooplankton “sloppy feeding,” viral lysis of bacteria and phytoplankton, and dissolution of detritus (Nagata 2000). The resulting products often exhibit a C-rich seasonal accumulation (Williams 1995), in which case export of this material is potentially an important route for C sequestration in the ocean. High C:N in marine DOM is likely due to phytoplankton extracellular release of organic C, with no associated N (Anderson and Williams 1998). This release may be a result of photosynthetic overflow under nutrient-limiting conditions, and so the highest relative rates are generally associated with oligotrophy (Teira et al. 2001). Another potential C-rich export route is via transparent exopolymer particles (TEP), which are polymeric gel particles that form abiotically from dissolved and colloidal organic matter. Although TEP do not sink gravitationally, they are exported as aggregates (Passow et al. 2001). Production rates of DOM and TEP are in general inversely related to nutrient supply. Nutrient loading could therefore change the internal system stoichiometry by decreasing this source of organic C—an example of where C sequestration is potentially inversely related to the supply of nutrients limiting primary production.

In addition to production of organic C, many marine organisms, including coccolithophorids, foraminifers, corals, and molluscs, produce calcium carbonate (CaCO₃). The ecology of these organisms is relatively poorly understood, and it is by no means clear how climate change will affect their competition with other algal groups. High abundance of these carbonate-forming biota has been associated with high N:P ratios (Tyrell and Taylor 1996), and so any shifts in these two elements, e.g., due to proliferation of nitrogen fixers or deposition of atmospheric N, could favor them. It is indeed somewhat enigmatic that N can be a major limiting element in the biosphere given the enormous amounts of N₂ in the atmosphere and the existence of N-fixing plants. Nitrogen is generally considered to be the “proximate limiting nutrient” in marine systems, representing local limitation according to Liebig’s law, while phosphate supplied by continental weathering and fluvial discharge is viewed as the “ultimate limiting nutrient” influencing system productivity on long time scales (Tyrell 1999). Shortfalls of N can be compensated for in the long term through N₂ fixation, although availability of trace elements, notably iron, and light limitation may limit this process (Martin 1990). This distinction between P and N as ultimate and proximate limiting factors is therefore far from clear-cut (Falkowski 2000). Deposition of macronutrients such as N, or micronutrients such as iron, from the atmosphere may have important impacts on the biological pump over long time scales. For example, nutrient supply is thought to have mediated variations in the sequestration of C, in the oceans that have accompanied glacial-interglacial cycles over the past two million years (Falkowski et al. 2000, Ganeshram et al. 2000). Understanding the role of iron in regulating C sequestration in the ocean presents a particularly difficult challenge for the scientific community. There are many poorly quantified processes relating to the cycling of iron in the ocean, notably the fraction of iron of aeolian origin that becomes soluble and bioavailable upon deposition in surface waters, and rates of biological uptake and scavenging (Wells et al. 1995, Johnson et al. 1997).

The stoichiometry of marine seston has been widely assumed to closely conform to the Redfield ratio of 106C:16N:1P (Redfield et al. 1963), which has proved to be particularly convenient for biogeochemical models. This assumption seems surprising given the diversity of processes described above. However, the C:N ratio of particulate organic matter in surface waters does not often deviate far from Redfield (e.g., Chen et al. 1996) and nutrient ratios in the deep ocean, reflecting long-term ratios of remineralization, are also close to the Redfield value (Anderson and Sarmiento 1994). The relatively constant Redfield ratios of dissolved nutrients and C in the deep ocean suggest that particles are exported in the same ratio, and that there is only a minor contribution from C-rich dissolved organics (Kühler and Koeve 2001). However, as already discussed, element ratios in phytoplankton can deviate significantly from Redfield (e.g., Daly et al. 1999), and it is well known that zooplankton (e.g., Gismervik 1997) and bacteria (e.g., Goldman et al. 1987) tend to have C:N ratios lower than the Redfield value. Geider and La Roche (2002) concluded that, both on the basis of laboratory C:N:P data and theoretical approaches to biochemical composition, there was little evidence to support the contention that the Redfield ratio reflects a physiological or biochemical constraint on the elemental composition of primary production, a conclusion also reinforced by Sterner and Elser (2002). Therefore, there is no a priori reason to believe that cycling and export must occur in Redfield proportions. Moreover, the C:N ratio of sinking particles is generally believed to increase with depth because of preferential remineralization of nutrient elements relative to C (Thomas et al. 1999). Although Redfield ratios have become an accepted empirical observation, a conceptual understanding of their biological and ecological basis is lacking (Falkowski 2000). Given that physiological constraints do not appear to be responsible, it must be that ecological feedback mechanisms including the regulation of total ocean N content involving...
nitrogen-fixing and denitrifying organisms are important. Nevertheless, any change in the C:nutrient ratio of export of organic matter could have a major bearing on C sequestration in the ocean (e.g., Heinze et al. 1991) and so this issue bears serious consideration in any attempt to model the ocean’s role in the C cycle simultaneous with an accounting of nutrient processing.

**Discussion**

Ecosystem responses reflect the net sum of processes at the cellular or organismal level and their interaction with abiotic factors in time and space. In both organisms and ecosystems the production efficiency in terms of C uptake and C sequestration depends strongly on the balance between intake of and demand for key nutrient elements. Nutrients like N or P will be recycled and reused by autotrophs, while excess C may either be oxidized to inorganic forms by the organisms themselves or heterotrophic decomposers, or be more permanently buried in sediment or soils. These similarities in feedbacks arise not because ecosystems mimic organismal allocation rules for C, N, or P, but because the interacting biota themselves that comprise ecosystems must obey stoichiometric rules at the level of their individual cells and bodies that greatly constrain the range of values that ecosystem-level pools and processes can attain. Thus, in the simplest scenarios, the fate or sequestration of C will be determined by the absolute and relative demands for C, N, and P of each organism relative to its resources. In food webs the largest discrepancy in element ratios is found between autotrophs and herbivores, causing low efficiency in the use of C (i.e., much C “in excess”). The evolutionary explanation for such a mismatch in element ratios between autotrophs and grazers may, from the autotroph’s perspective, be seen as an adaptation to cause lower grazer fitness (at some expense to its own growth, however; cf. Moran and Hamilton 1980, White 1993), while the grazers dilemma appears to be a trade-off between rapid growth and the risk of nutrient limitation. This trade-off appears to exist because of a general link between high levels of key nutrients (especially P), high levels of important macromolecules (e.g., P-rich ribosomal RNA), and growth rate (Elser et al. 2000, Vrede et al. 2002, 2004). Thus, high and low body levels and demands for P (and to a lesser extent N) in consumers may be seen as stoichiometric manifestations of evolutionary adaptations along the classic r–K axis. In any case, these inexorable constraints mean that herbivores rarely find optimal food, and that stoichiometrically imbalanced autotroph production is allowed to go elsewhere.

To the extent that other organisms in the ecosystem remain limited by inadequate sources of fixed energy, one should expect strong selective pressure towards utilization of this excess C. Autotrophs may allocate this excess C to C-rich compounds such as structural matter or exudates for various purposes such as digestive screens (algae) or grazer repellents. Under pressure from selective grazers, it could also pay to maintain high C:N or C:P ratios in grazable tissue to reduce the risk of its consumption and/or to depress grazers (cf. White 1993). However, this strategy would not work in communities with nonselective grazers (e.g., aquatic systems dominated by filter feeders) unless some group-selection argument is invoked for the phytoplankton community. Excess C in the form of carbohydrates, and exchange of carbohydrates and nutrients, could also be seen as a stoichiometric basis for the ecological stabilization and evolution of symbiosis (cf. Berman-Frank and Dubinsky 1999, Sterner and Elser 2002, Kooijman et al. 2004).

Following the same line of reasoning, one could argue that the organisms that comprise ecosystems occupy different stoichiometric niches. The ability to explore extremely C-rich (and stoichiometrically unbalanced) food like woody material and phloem implies that organisms such as fungi, termites, wood lice and aphids have evolved to use major sources of energy that for other organisms would be largely inadequate or inaccessible due to nutrient imbalance. Such adaptations could involve gut symbionts and sophisticated means to metabolically reclaim N (as in termites; Higashi et al. 1992), the ability to flux large amounts of unutilized organic carbon (e.g., honeydew production by aphids), or the development of reduced body demands for limiting elements (Fagan et al. 2002, Jaenike and Markow 2003). This again would have consequences for growth rates and life-cycle strategies. A stoichiometric niche could also mean that organisms spatially prefer some more stoichiometrically adequate areas to others. At a small scale this could mean preference for the tip of buds rather than mature leaves for herbivorous insects; at a larger scale it could imply migration of ungulates to seek the most nutritious herbs (White 1993, van der Wal et al. 2000).

At an even larger scale, the length and stability of food chains could also be determined by stoichiometric principles (Hastings and Conrad 1979, Hairston and Hairston 1993). As argued by Hastings and Conrad (1979), an evolutionarily stable strategy for food chains would imply that food chains should collapse to the shortest possible length compatible with biochemical and physiological constraints (usually three steps). Thus, the assumption that is it the trophic structure that controls the fraction of energy consumed at each trophic level, rather than the energetics controlling trophic structure (Hairston and Hairston 1993) may indeed be questioned when seen from a stoichiometric point of view.

To extrapolate from organisms to ecosystems may be a dubious process, but the processes described above may also impinge on large-scale ecosystem properties. The unavoidable imbalances between autotrophs and consumers appear to have the net effect that overall
transfer of primary production to higher trophic levels is impaired under conditions of nutrient-limited autotroph production. As a result, much C can be sequestered in standing biomass of nutritionally unsuitable autotroph biomass with high C:nutrient ratio. This further affects the fate of production by increasing the percentage of production entering detrital pools to be entrained into slow detrital food webs, where the efficiency of C processing is low due to the detritus’ low nutrient content. This is illustrated by the cross-ecosystem comparison of Cebrían (1999). Systems dominated by autotrophs with low C:element ratios and fast turnover rates such as phytoplankton communities are effectively grazed and little C is sequestered to recalci-trant detrital pools, while terrestrial systems dominated by high C:element ratios and low turnover sequester most of the fixed C as detritus.

The balance of carbon fixation by photosynthesis and release by oxidation processes is the basis of the global C cycle. The principles of this cycle have been known for a long time, yet the various factors regulating this balance and dynamics are still imperfectly understood (Falkowski et al. 2000). In a global-change context, an understanding of the parameters regulating the sequestration and net balance of C in ecosystems is imperative (Giardina and Ryan 2000, Grace and Rayment 2000). Although the cumulative effects of anthropogenic C emissions are implicated as the primary cause of increased atmospheric CO₂ concentrations, other ecosystem processes still account for some 95% of the fluxes. Importantly, cycling of C occurs in tandem with nutrient elements such as N and P both of which have also been subject to major changes in biogeochemical cycling (Falkowski et al. 2000). As described above, the efficiencies with which different elements are cycled or sequestered in organisms and ecosystems depend on their relative availabilities. Thus, major changes in fluxes of C to and from the atmosphere may be induced by relatively subtle shifts in the C:nutrient ratios of particular pools or in the relative importance of different pools having different C:nutrient ratios. Since global perturbations of nutrient cycles are much larger than current anthropogenic impacts on C cycling (Falkowski et al. 2000), a better understanding of how nutrient cycles interact with C cycling is imperative. While following the balance of multiple elements in individual organisms and its implications for specific ecological interactions are reasonably straightforward, application of stoichiometric principles at larger scales should also help greatly in understanding the fate of fossil-fuel C and its interactions with anthropogenic impacts on limiting nutrient availability. Following the axiom of Liebig limitation, one simple implication of these principles in a global context is that biospheric storage of C is limited relative to current levels of C release to the atmosphere because C:N and C:P ratios in C sources (fossil fuels) are much larger than the ratios in potential modern sinks (Peterson and Melillo 1985, Sterner and Elser 2002). Whether or not such extrapolations are accurate upon closer examination, it seems likely that a better understanding of the biological coupling of multiple chemical elements in evolving biota will improve our ability to predict the future dynamics of the biosphere under an increasing anthropogenic influence and to understand the consequences of those changes for diverse ecosystems.

Acknowledgments

DOH acknowledges the European Science Foundation for supporting the workshop leading up to this Special Feature. T.R. Anderson is funded by the Natural Environment Research Council. U.K. J. Elser acknowledges NSF Integrated Research Challenges for Environmental Biology Grant DEB-9777847.

Literature Cited


Caron, D. A., and J. C. Goldman. 1988. Dynamics of pro-
testican carbon and nutrient cycling. Journal of Protozoology
35:247–249.

Cebrian, J. 1999. Patterns in the fate of production in plant


response of dietary phosphorus deficiency on the abundance, phos-


and stoichiometric analysis. Thermochimica Acta 309:121–
128.


Elser, J. J., M. Elser, N. A. Mackay, and S. Carpenter. 1995. Plankton-mediated transitions between N-lim-


response to seston phosphorus enrichment. Ecology 82:898–
903.

Elser, J. J., and J. Urabe. 1999. The stoichiometry of con-

Enriquez, S., C. M. Duarte, and K. Sand-Jensen. 1993. Pat-
terns in decomposition rates among photosynthetic organ-

205–214.


Falkowski, P. G. 2000. Rationalizing elemental ratios in uni-

our knowledge of Earth as a system. Science 290:291–
296.

Follows, M. J., R. G. Williams, and J. C. Marshall. 1996. The solubility pump of carbon in the subtropical gyre of
630.

Toward an allocation scheme for global terrestrial carbon

Galloway, J. N., W. H. Schlesinger, H. L. Levy, A. Michaels,
and J. L. Schnoor. 1995. Nitrogen fixation: an anthropo-
genic enhancement–environmental response. Global Bi-

Ganeshram, R. S., T. F. Pedersen, S. E. Calvert, G. W.
variability in denitrification in the world’s oceans: causes and consequences. Paleoenageography 15:361–376.

Geider, R. J., and J. La Roche. 2002. Redfield revisited: vari-
ability of C:N:P in marine microalgae and its biochemical


Gismervik, I. 1997. Stoichiometry of some marine planktonic

Goldman, J. C., D. A. Caron, and M. R. Dennett. 1987. Regu-
lation of gross growth efficiency and ammonium regen-
eration in bacteria by substrate C:N ratio. Limnology and
Oceanography 32:1239–1252.

Goldman, J. C., J. J. McCarthy, and D. G. Peavey. 1979. Growth rate influence on the chemical composition of phy-

Goldman, J. C., and D. G. Peavey. 1979. Steady-state growth
and chemical composition of the marine chlorophyte Dun-
taliella tertiolecta in nitrogen-limited continuous cultures.
Applied Environmental Microbiology 38:894–901.

Gorissen, A., J. H. van Ginkel, J. B. Keurentjes, and E. A.
van Veen. 1995. Grass root decomposition is retarded when
grass has been grown under elevated CO2. Soil Biol. Bioch-
em. 27:117–120.


Griffiths, B. S., K. Ritz, R. D. Bardgett, R. Cook, S. Chris-
tensen, F. Ekelund, S. J. Sørensen, E. Bäåth, J. Bloem, P.
C. de Ruiter, J. Dolling, and B. Nicolardot. 2000. Ecosys-
tem response of pasture soil communities to fumigation-
induced microbial diversity reductions; an examination of
the biodiversity–ecosystem function relationship. Oikos
90:279–294.


White, T. C. R. 1993. The inadequate environment: nitrogen and the abundance of animals. Springer-Verlag, New York, New York, USA.

Williams, P. J. le B. 1995. Seasonal accumulation of carbon-rich dissolved organic material, its scale in comparison with changes in particulate material and the consequential effect on net C:N assimilation ratios. Marine Chemistry 51:17–29.