

Research review

Stoichiometric flexibility as a regulator of carbon and nutrient cycling in terrestrial ecosystems under change

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Summary

Ecosystems across the biosphere are subject to rapid changes in elemental balance and climatic regimes. A major force structuring ecological responses to these perturbations lies in the stoichiometric flexibility of systems – the ability to adjust their elemental balance whilst maintaining function. The potential for stoichiometric flexibility underscores the utility of the application of a framework highlighting the constraints and consequences of elemental mass balance and energy cycling in biological systems to address global change phenomena. Improvement in the modeling of ecological responses to disturbance requires the consideration of the stoichiometric flexibility of systems within and across relevant scales. Although a multitude of global change studies over various spatial and temporal scales exist, the explicit consideration of the role played by stoichiometric flexibility in linking micro-scale to macro-scale biogeochemical processes in terrestrial ecosystems remains relatively unexplored. Focusing on terrestrial systems under change, we discuss the mechanisms by which stoichiometric flexibility might be expressed and connected from organisms to ecosystems. We suggest that the transition from the expression of stoichiometric flexibility within individuals to the community and ecosystem scales is a key mechanism regulating the extent to which environmental perturbation may alter ecosystem carbon and nutrient cycling dynamics.

Stoichiometric flexibility across scales

Stoichiometric relationships underpin the structuring of biological systems. These relationships differ systematically from molecules to ecosystems, reflecting the variation in biological functions and biochemical limitations (Sternner & Elser, 2002). Because all organisms must meet their basic metabolic requirements, biotic interactions are both regulated by and also feed back to their environment's resource availability (Elser *et al.*, 1996). Therefore, a system's response to environmental change, from gene expression to macro-scale processes, will ultimately be constrained by its ability to adjust to shifting elemental balances — its stoichiometric flexibility.

Anthropogenic impacts on the Earth's climate, energy and element cycles (Table 1) include global-scale alterations in nitrogen (N) and phosphorus (P) cycling: more than doubling the available N inputs into the biosphere via fertilizer manufacture and redistributing mined P across the Earth (Falkowski *et al.*, 2000). As N and P commonly limit primary producers

(Elser *et al.*, 2010; Harpole *et al.*, 2011; Marklein & Houlton, 2012), such massive perturbations are expected to have stoichiometric consequences across food webs. The rapid shift in the bioavailability of essential elements, coupled with increasing atmospheric CO₂ and warming (Raupach *et al.*, 2007), can alter the stoichiometric relationships of biological systems at multiple scales. For example, because rapidly growing organisms require the coupled use of N- and P-rich resources to meet high demands for RNA and protein, nutrient enrichment may select for species with high growth rates, ultimately shifting the community composition and, potentially, ecosystem function (Smith, 1983; Chapin *et al.*, 1986; Mack *et al.*, 2004; Marklein & Houlton, 2012).

The increase in anthropogenically caused environmental perturbations has provoked interest in understanding how stoichiometric relationships control responses to disturbances. Organisms generally have conservative stoichiometries relative to the elemental heterogeneity of their environment (Moe *et al.*, 2005), such that the acquisition of carbon (C), N and P

Table 1 Anthropogenic perturbations to global chemical cycles based on mid 1990s data. Adapted from Falkowski *et al.* (2000)

Element	Form of change	Processes (approximate contribution to total flux in parentheses)	Anthropogenically-driven % change
C	CO ₂ release to atmosphere from organic matter oxidation	Terrestrial respiration and organic matter decay as CO ₂ (88%); fossil fuel combustion and land-use (12%)	13
N	Conversion to biologically-available forms from N ₂	Natural biological fixation (48%); fixation from agricultural production, fossil fuel production, and fertilizer production (52%)	108
P	Redistribution of biologically-available forms through mining	Chemical weathering (20%); mining (80%)	400

constrains both the individual and community response to perturbation. Biological systems may demonstrate strict homeostasis, in which element ratios are fixed (Sturner & Elser, 2002). From the organismal to community state, strict homeostasis will drive the most limiting resource (in terms of supply rate, although not necessarily concentration) to regulate productivity (Rastetter & Shaver, 1992). Alternatively, systems might be stoichiometrically plastic, shifting their elemental balance in response to perturbation (Sturner & Elser, 2002). At the organismal level, this can be manifested by an adjustment in growth form or tissue allocation patterns. For example, temperate forest hardwoods have been shown to increase their relative investment to woody biomass with greater N availability (Melillo *et al.*, 2011). At larger scales, changes in community composition and trophic interactions can alter the stoichiometric composition of an ecosystem. This phenomenon can occur with succession or invasions, and may be driven by abiotic perturbations (e.g. nutrient or warming-driven shrub expansion into sedge-dominated tussock tundra) (Chapin *et al.*, 1986; Mack *et al.*, 2000; Walker *et al.*, 2006).

The expression of stoichiometric plasticity will be regulated both by the nature of the perturbation and the costs associated with change. At the organismal level, primary producers tend to be more stoichiometrically flexible than their consumers (Hessen *et al.*, 2004). For example, plants can shift tissue allocation towards more woody biomass (molar ratio C : N : P \approx 7900 : 25 : 1; Vitousek *et al.*, 1988) than leaf tissue (C : N : P \approx 1212 : 28 : 1; McGroddy *et al.*, 2004). Plant stoichiometric flexibility also stems from their nutrient resorption capacity, with senescing leaves resorbing > 60% of leaf N and P (Vergutz *et al.*, 2012), increasing litter C : X relative to green foliage (litter C : N : P = 3007 : 45 : 1) (McGroddy *et al.*, 2004).

The stoichiometric flexibility of terrestrial plants reflects their physiological capacity to accumulate and store elements in excess of their immediate needs, to adjust allocation towards the synthesis of more C- or nutrient-rich compounds, and to alter growth form towards defense, storage and structural tissues. By contrast, consumers tend to have more fixed tissue partitioning (Anderson *et al.*, 2005). As consumers are less stoichiometrically plastic because of greater physiological constraints on allocation,

stoichiometric shifts in primary producers can regulate the composition and behavior of herbivore and decomposer communities, and the ecological processes they carry out (Hessen *et al.*, 2004; Sardans *et al.*, 2011).

Ecosystems may therefore be stoichiometrically flexible by two connected mechanisms. First, by *varying stoichiometry within individuals*: organisms can alter allometric patterns and tissue chemistry to adjust their overall stoichiometry (Sturner & Elser, 2002). Second, by *shifting dominance among organisms that differ in their average stoichiometry*: the composition of key guilds and their functions can change (e.g. altered consumer pressures, competitive interactions amongst guilds or trophic group, invasion potential; Moe *et al.*, 2005).

Variation in the C : N : P range of organisms and their biological components is generally greater than that in the systems that they build (Table 2). Although stoichiometry may vary significantly within or amongst organisms and across trophic groups, the chemically coupled feedbacks between primary producers, heterotrophs and their abiotic environment suggest that biota in terrestrial ecosystems will tend towards relatively convergent C : N : P ratios when moving from local to global scales (Elser *et al.*, 2010). These patterns emerge when comparing variation in microbial and phytoplankton C : N : P from the macromolecules building individuals to communities (Goldman *et al.*, 1979; Geider & La Roche, 2002; Hall *et al.*, 2011), and to global scales (Cleveland & Liptzin, 2007), and in plant C : N : P relationships from biomes to the global scale (Vitousek *et al.*, 1988; Reich & Oleksyn, 2004; McGroddy *et al.*, 2004). To accurately quantify the impacts of stoichiometric flexibility (or lack thereof) on ecosystem processes, researchers must identify where and to what extent the potential for stoichiometric change exists across biologically relevant scales (Fig. 1).

Ecosystem processes, such as C or N storage, are emergent properties that result from interactions of organisms with the abiotic environment. Organisms may themselves reflect stoichiometric variation across scales, both through shifts in the physiological state of individuals (e.g. increasing woody biomass production relative to other tissues) and/or the biotic structuring of communities (e.g. shrub invasion into grasslands). Therefore,

Table 2 Example of stoichiometric ranges for C : N, C : P and N : P (expressed in atomic molar ratios) for different biological states, increasing in scale from sub-cellular components to single celled planktonic organisms, and from terrestrial plant tissues to whole forest biomass. Note that these ranges represent potential molar ratios, but not the concentration of the component (e.g. percent of a cell that is DNA) contained within its larger biological state (e.g. a cell)

Biological state	C : N	C : P	N : P	Source
Common subcellular components (e.g. nucleotides, RNA, DNA, amino acids, fatty acids, carbohydrates, chitin, chlorophyll)	c. 0.5 (e.g. cystine) to > 80 (e.g. phosphoglycerides) to ∞ (no N; e.g. carbohydrates, waxes, sterols, fatty acids)	< 5 (e.g. DNA, RNA) to > 15 (e.g. phosphoglycerides) to ∞ (no P; e.g. nucleotides, waxes, chitin, chlorophyll)	< 0.2 (e.g. phosphoglycerides) to < 2 (e.g. RNA) to ∞ (no P)	Geider & La Rouche (2002)
Marine phytoplankton (range reflects decreasing P resource supply and growth rate in P-limited culture of <i>Monochrysis lutheri</i>)	7.1–11.3	106–1300	15–115	Goldman <i>et al.</i> (1979)
Forest components: subalpine to tropical forest biomes (foliage, woody tissue, roots)	26 (foliage, fertile site) to 505 (woody tissue)	800 (foliage, fertile site) to 12197 (woody tissue)	11 (root) to 57 (foliage, infertile sites)	Vitousek <i>et al.</i> (1988)
Total forest biomass	134–299	3043–6241	17–25	

both within and across scales, the expression of potential stoichiometric range will vary with the biological composition of systems. Recognizing that ecological processes are not necessarily the direct sum of their parts, we will explore how the plasticity of macro-scale ecosystem processes is regulated by the stoichiometric flexibility of the organisms that generate them. A consideration of how the cross-scale structuring of stoichiometric relationships influences responses to perturbation spurs several key questions:

- How does the expression of stoichiometric flexibility at one scale influence the expression of stoichiometric flexibility among linked systems?
- Is there a correlation between the biological state of either individuals or communities (e.g. physiological and ontogenetic condition, successional status) and susceptibility to stoichiometric perturbation?

- What mechanisms regulate whether a perturbed system returns to its initial stoichiometric condition, or shifts towards an alternative stable state (Beisner *et al.*, 2003)?
- What are the consequences of these responses for macro-scale biogeochemical processes, such as terrestrial C sequestration potential?

An understanding of how the stoichiometric flexibility of organisms within ecosystems influences the system's overall stoichiometric plasticity, and how this varies across systems, is a key component to the accurate prediction of ecological responses to perturbation using a stoichiometric framework. These questions, however, are more readily posed than answered, partly because studies often use different methodologies (Mikkelsen *et al.*, 2008), and partly because they rarely directly address stoichiometric changes among interacting ecosystem components in response to perturbation (Moe *et al.*, 2005). This lack of focus

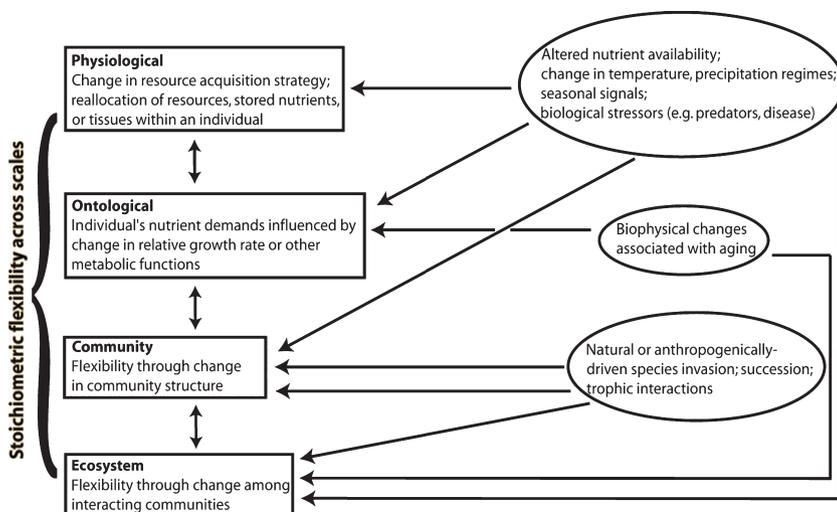


Fig. 1 Schematic representation of the ways in which stoichiometric flexibility may be expressed in ecosystems and in their component parts (boxes). Each type of stoichiometric flexibility can be directly or indirectly influenced by the other states. Similarly, drivers (ovals) may influence stoichiometric relationships at multiple scales simultaneously.

on stoichiometric flexibility reflects both the wide array of conditions under which elemental plasticity can occur in biological systems, and the lack of a coherent framework under which stoichiometric flexibility is identified.

Although a definitive synthesis on the role of stoichiometric flexibility in response to global change may be impossible at present, we can identify potential insights and limits of the application of this theoretical framework for the exploration of the responses of terrestrial systems to global change stressors. We suggest that integrating field measurements into coupled-element models that overtly address stoichiometric flexibility might better inform projections of ecosystem dynamics, relative to those derived using short-term, small-scale and single-factor manipulation studies.

Stoichiometric flexibility and the structuring of terrestrial ecosystems

Differences in the demand and competitive ability of plants for elements within heterogeneous soil environments are key forces structuring terrestrial communities. This concept stems from the 19th century observations of Sprengel and Liebig that mismatches in the supply of and demand for nutrients drive resource limitation and regulate the growth of individual plants (van der Ploeg *et al.*, 1999). Scaling up, cross-ecosystem comparisons of C : N : P ratios should reflect selection for the efficient use of the most limiting nutrient. For example, a global comparison of forest foliar C : N : P demonstrates that the abundance of P relative to C and N correlates with the variation in P availability at the biome level, consistent with selection for efficient foliar P use (McGroddy *et al.*, 2004).

Such cross-scale stoichiometric relationships in terrestrial systems are challenging to identify because of their patchy resource distributions and broad spectrum of autotrophic growth forms (Cleveland & Liptzin, 2007). In general, the wide range of C : element ratios among plant tissues is driven by the C-rich compounds needed for structural support and defensive chemicals. For example, chemically recalcitrant lignocellulose woody tissues contain only 0.01–0.1% N by weight, as opposed to the typical 1–5% N of herbaceous tissues (Cowling & Merrill, 1966). As a result, heterotrophs face an enormous diversity of plant-derived organic compounds that differ in their underlying elemental ratios, driving a substantial range of heterotrophic substrate use efficiency (SUE; the fraction of consumed molecules converted into biomass; Sterner & Elser, 2002).

Plant stoichiometry thus creates the 'boundary conditions' for heterotrophic productivity. Organisms cannot produce more biomass than allowed by the supply rate of their most limiting resource, but the specific chemistry of plant compounds controls where, within these stoichiometric boundaries, consumer groups operate. The efficiency with which heterotrophs can use plant chemicals varies widely, with SUE approaching 70% for bacteria using plant sugars (Sugai & Schimel, 1993) vs 0% for most animals eating lignocellulose. In the transfer of energy from plants to their consumers, C : N : P ratios shrink and the stoichiometric ranges contract (Sterner & Elser, 2002). Therefore,

heterotrophs characteristically live in a C-rich, nutrient-poor world relative to their requirements. This elemental mismatch between primary producers and their consumers drives an imbalance between resource supply and demand that limits an ecosystem's rate of C and nutrient transfer among trophic levels (Sterner & Elser, 2002).

Within the heterogeneous soil environment, as detritus C : N approaches that of its decomposers, microbes shift from nutrient immobilization to mineralization, thereby regulating plant-available nutrients (Manzoni *et al.*, 2008). Regardless of the absolute decomposition rate, decomposers retain or release nutrients based on their elemental needs relative to resource supply (Manzoni *et al.*, 2008). Although the stoichiometric regulation of decomposers operating in a coupled feedback with plants over relatively small spatial and temporal dimensions shapes ecosystem processes and structures at the community level (Chapin *et al.*, 1986), terrestrial stoichiometries tend to be conserved relative to local environmental heterogeneity over large scales (e.g. the cross-biome variation of the C : N, C : P and N : P foliar and soil microbe nutrient ratios is lower or equal to the within-biome level variation; McGroddy *et al.*, 2004; Cleveland & Liptzin, 2007).

Supporting these Redfield-like patterns of terrestrial biota are observations that, although soil microbial biomass C, N and P concentrations vary globally over several orders of magnitude (5–2500 $\mu\text{mol kg}^{-1}$ soil, 1–178 $\mu\text{mol kg}^{-1}$ soil and 0.1–14 $\mu\text{mol kg}^{-1}$ soil, respectively), microbial biomass C : N : P ratios are conserved at a global scale (C : N average = 8.6 ± 0.3 , N : P average = 6.9 ± 0.4 ; Cleveland & Liptzin, 2007). This result parallels the findings of McGroddy *et al.* (2004) that, despite biome-level differences trending towards greater foliage N : P with decreasing latitude (reflecting that P is a primary limiting nutrient in older tropical soils and N is the dominant limiting nutrient in younger temperate and high-latitude soils; Reich & Oleksyn, 2004), forest leaf C : N : P ratios are broadly constrained worldwide (C : N average = 43.6 ± 3.5 ; N : P = 27.8 ± 1.4). Further, although total soil C, N and P content varies globally by orders of magnitude (e.g. total soil C ranges nearly 40-fold, from 1108 to 39 083 mmol kg^{-1}), soil C : N : P ratios are markedly constrained at the global scale (log-normal molar C : N range from 2 to 30, N : P range from 1 to 77; Cleveland & Liptzin, 2007), suggesting a tight stoichiometric coupling between decomposers and their soil environment.

Changes in nutrient availability or litter chemistry may alter microbial dynamics, driving stoichiometric feedbacks between primary producers, their consumers and decomposers within ecosystems and at local scales. For example, although soil microbial biomass C and total soil C are positively correlated over large scales, microbial N : P appears to follow relatively strict homeostatic control: it does not vary with latitude nor does it correlate with soil N : P supply ratios. This pattern suggests that sufficient relative N and P availability is necessary to maintain microbial N : P stoichiometry, with greater N and P supporting greater microbial C (Cleveland & Liptzin, 2007).

The observation of relatively strict microbial N : P homeostasis correlates with the observation that P often appears to limit

microbial biomass and activity in low-latitude, P-poor ecosystems (Cleveland *et al.*, 2006; Townsend *et al.*, 2007), whereas N seems to limit soil microbes in high-latitude, N-poor organic soil systems (Lavoie *et al.*, 2011; Sistla *et al.*, 2012). In both cases, *in situ* fertilization with the limiting resource stimulates microbial activity, amplifying soil decomposition (Mack *et al.*, 2004; Cleveland & Townsend, 2006). Intriguingly, fertilization significantly stimulates soil C losses and increases plant C gain (by facilitating shrub expansion), whilst driving a net C and N loss in the Arctic system by accelerating decomposition (Mack *et al.*, 2004). This phenomenon highlights that, in systems in which the same nutrient stoichiometrically constrains both plant and microbial productivity, alleviation of the limiting nutrient may drive divergent patterns in plant and soil C storage – and, potentially, a net loss of the added element. Therefore, depending on the strength of the stoichiometric linkages among a system's components, including their degree of stoichiometric homeostasis and nutrient limitation, the expression of stoichiometric flexibility in response to environmental stressors can significantly alter – or help to maintain – macro-scale states and processes.

Stoichiometric flexibility and terrestrial responses to global change

Despite several decades of global change research, the impacts of climate warming, elevated atmospheric CO₂ (eCO₂) and altered nutrient availability on terrestrial C dynamics have remained surprisingly difficult to predict, at least in part reflecting the complexity of the coupling between C and nutrient cycles (Rastetter *et al.*, 1997). Stoichiometric responses to perturbation are intrinsically tied to altered resource limitation. Because these disturbances impact nested biological systems, approaching global change questions with a stoichiometric flexibility perspective may provide deeper insights into the feedbacks between environmental perturbation and ecosystem responses over time.

Varying from sub-cellular investigations to ecosystem-level manipulations, numerous studies have shown that warming, eCO₂, N and P fertilization can drive stoichiometric change (Elser *et al.*, 2010). Although global change phenomena inherently involve coupled shifts in resource availability and climate, global change experiments often focus on single drivers. While imperfect, such experiments help to collapse the complexity in identifying the potential range of a system's stoichiometric flexibility, including the stoichiometric feedbacks, thresholds and the mechanisms underlying them.

Changes in the chemical composition of plants and/or decomposers will inevitably have consequences for the other trophic levels to which they are biogeochemically coupled, scaling up to macro-processes such as ecosystem C storage. Thus, global change drivers can affect both directly and indirectly each of the connected axes of nutrient cycling, primary productivity and community structure (Elser *et al.*, 2010). Because stoichiometric flexibility will vary across ecosystem components, the identification of stoichiometric constraints and linkages among components is critical to projecting the responses of terrestrial systems to environmental change.

A major challenge in the application of a stoichiometric flexibility perspective to global change questions is scaling between stoichiometric responses measured over different spatial and temporal scales. A classic example of this phenomenon lies in the conflicting responses to eCO₂ moving from the leaf to the ecosystem scale. At the molecular level, eCO₂ stimulates photosynthesis by increasing the carboxylation rate of N-rich Rubisco, whilst competitively inhibiting photooxidation (Drake *et al.*, 1997). Scaling to the leaf level, plants regulate the greater N demand by increasing leaf-level C : N, partly by down-regulating Rubisco synthesis. Although this limits the eCO₂-driven increase in photosynthesis, leaf-level net C gain generally remains elevated. Therefore, eCO₂ might be expected to scale up to increase net primary productivity (NPP) and potentially, net ecosystem C storage capacity. However, eCO₂ response patterns vary at the ecosystem level, ranging from net C gain to no net change (Ainsworth & Long, 2005; Norby & Zak, 2011).

Variation in net C storage under eCO₂ therefore tends to increase with scale, with predictable cellular-level C gain not necessarily translating to ecosystem C gain. Biological differences in the stoichiometric regulation of response to eCO₂ when scaling from cells to ecosystems creates dissonance in predicting the integrative macro-scale process of net C storage based on leaf-level responses. This phenomenon reflects the fact that the sequestration of more ecosystem C requires plants and soils to be able to store more C, and that the system must have the nutrients necessary for plants to make molecules that can be sequestered (Rastetter *et al.*, 1992). Therefore, the identification of the key mechanisms regulating stoichiometric flexibility, with a focus on nutrient availability and allocation patterns, will allow researchers to better model plausible macro-scale consequences of global change phenomena. With this perspective, we consider terrestrial responses to global change perturbations, highlighting mechanisms that limit the translation of stoichiometric flexibility across biological states.

Organismal-level stoichiometric flexibility

A common plant response to both eCO₂ and warming is a faster growth rate. For example, young trees with expanding canopies and exponential growth often have greater growth responses to eCO₂ than older stands, including increasing leaf area and NPP (Hättenschwiler *et al.*, 1997; Norby *et al.*, 2001). Because rapidly growing organisms have increased anabolic rates, and thus require more nutrients per unit biomass C than slower growing organisms, faster growth is stoichiometrically regulated by increased N and P demands relative to C (Hall *et al.*, 2011; Harpole *et al.*, 2011; Marklein & Houlton, 2012). Linking ontogeny and environmental stressors to plant stoichiometric flexibility at the metabolomic level, Rivas-Ubach *et al.* (2012) demonstrated that the stimulation of growth decreases leaf-level C : nutrient and N : P ratios, whilst increasing primary metabolite content.

Nitrogen, in particular, has long been noted to be a stoichiometric regulator of the potential for increased NPP gain with eCO₂

or warming, because the redistribution of N from relatively low C : N soil pools to high C : N plant tissues can increase C sequestration. CO₂ fertilization can drive increased woody growth in established individuals (Hamilton *et al.*, 2002; Finzi *et al.*, 2002) and promote increased woody plant dominance (Souza *et al.*, 2010). The sequestration of N in high C : N recalcitrant tissues and soil organic matter (SOM) may reduce plant-available N by retarding decomposer activity over time, however, and ultimately reduce plant growth (Luo *et al.*, 2006). As such, if the production and use of photosynthate is nutrient limited, the effect of eCO₂ (Hu *et al.*, 2001; de Graaff *et al.*, 2006) or warming (Hobbie *et al.*, 2001; Rustad *et al.*, 2001; Melillo *et al.*, 2011) on plant growth will be constrained.

There is evidence that eCO₂-driven N limitation may occur in both forests and perennial grasslands (Hu *et al.*, 2001; Reich *et al.*, 2006; Norby *et al.*, 2010; Garten *et al.*, 2011), including a decline in the stimulation of NPP coupled with increasing plant N deficiency (Norby *et al.*, 2010) and greater microbial N immobilization (Hu *et al.*, 2001) in experimental systems. Plants may initially compensate for greater N demand by expanding their exploration of the soil through increased allocation to roots, producing greater fine root biomass and rooting more deeply (Luo *et al.*, 2006; Iversen *et al.*, 2008). As plants expand their root systems, however, more N is committed to long-lived woody structures that decompose slowly and immobilize N, reducing N availability over time. The increasing accumulation of recalcitrant, high C : N litter has been hypothesized to inhibit decomposer activity, thus limiting the ability of plants to respond to eCO₂ (Luo *et al.*, 2006). Therefore, although the development of N limitation under eCO₂ will be controlled by plant–soil–microbe feedbacks, alleviating this limitation will depend on a net increase in N at the ecosystem-scale (Rastetter *et al.*, 1997).

In contrast with eCO₂-driven N limitation, warming can act as a positive feedback that promotes woody encroachment in nutrient-poor systems by stimulating decomposer activity and N mineralization (Sturm *et al.*, 2008; Melillo *et al.*, 2011). For example, a multi-year warming experiment in an N-limited temperate forest enhanced N mineralization sufficiently to support C gain in woody biomass, nearly compensating for belowground soil C loss (Melillo *et al.*, 2011). Intriguingly, although soil warming experiments in a variety of ecosystems have driven short-term increases in soil respiration, the response tends to decline over several years (Rustad *et al.*, 2001; Allison *et al.*, 2010; Melillo *et al.*, 2011). This acclimation may be driven by a decline in microbial C use efficiency (CUE; the ratio of biomass synthesis to C uptake) which governs biomass C : X elemental relationships in response to altered environmental or physiological conditions (Allison *et al.*, 2010). In the short term, reduced CUE can be caused directly by thermal stress and the depletion of labile, high-SUE compounds, or indirectly via longer term plant–microbe feedbacks that alter microbial community composition (Allison *et al.*, 2010). Therefore, warming may drive decomposer nutrient-limitation over time, acting as a negative feedback to the initial acceleration of decomposition and ultimately, plant growth.

In extremely nutrient-limited systems, such as Arctic and boreal ecosystems, N (and to a lesser extent available P) most commonly limits NPP (Shaver & Chapin, 1986; Hobbie *et al.*, 2001). Over the decadal time frame, woody plant growth in Arctic systems is strongly responsive to experimental air warming, N and P fertilization, and ongoing climate warming (Mack *et al.*, 2004; Sturm *et al.*, 2008; Myers-Smith *et al.*, 2011). Greater N availability, in particular (through both fertilization and indirectly via warming), stimulates plant N sequestration (Natali *et al.*, 2012), increasing woody biomass production and dominance in tundra systems (Rundqvist *et al.*, 2011; Myers-Smith *et al.*, 2011).

The acceleration of woody biomass synthesis with greater N uptake is tied to the ability of certain shrub species to shift their allocation patterns towards structural branch production (Bret-Harte *et al.*, 2002). Warming also promotes directly woody expansion over time by lengthening the growing season, whilst stimulating shrub growth rate and fine root production, increasing their ability to both acquire N and capture C used in secondary stem biomass production (Hobbie & Chapin, 1998; Bret-Harte *et al.*, 2002; Walker *et al.*, 2006; Sullivan *et al.*, 2007). Therefore, if allocation to woody biomass increases at the ecosystem level with warming, the redistribution of a relatively small proportion of soil N can significantly promote long-term C storage (McKane *et al.*, 1997; Melillo *et al.*, 2011).

Community-level stoichiometric flexibility

Warming, eCO₂ and fertilization can independently drive stoichiometric change at the organismal level, potentially altering macro-scale processes. At the community level, plant stoichiometric flexibility may be expressed through shifts in stand establishment and composition towards woody dominance (Mack *et al.*, 2004; Souza *et al.*, 2010; Melillo *et al.*, 2011). Conversely, fertilization may facilitate a positive feedback between rapidly growing plants and soil nutrient availability (Chapin *et al.*, 1986). For example, in nutrient-poor ecosystems, invasion by fast-growing (high nutrient-demand) species may drive a positive feedback through a combination of less conservative plant nutrient use efficiency, increased deposition of nutrient-rich litter, and faster SOM turnover (Hobbie, 1992; Allison & Vitousek, 2004). In contrast with greater C sequestration due to N mobilization allocated towards producing relative high C : N tissues like wood, such a trajectory would probably drive a more rapidly cycling, lower C : nutrient community (Hobbie, 1992) potentially reducing net C storage.

Relatively small-scale shifts among interacting plant and microbial communities can also feed back through changes in both resource inputs and demand to regulate macro-scale nutrient cycling dynamics. For instance, the invasion of *Morella faya* (formerly *Myrica faya*) with its N-fixing root symbionts (*Frankia* spp.) in N-poor volcanic Hawaiian soils stimulated N mineralization rates (increasing the supply of available N by more than four-fold), litterfall production and soil organic C stocks in densely colonized areas (Vitousek & Walker, 1989; Asner *et al.*, 2009). Paralleling this greater N availability, N oxide (N₂O) and

NO) emissions increased by 16-fold (or $296 \pm 1.5 \text{ kg N yr}^{-1}$) under wet conditions in densely invaded areas (Hall & Asner, 2007). Invasion by *M. faya* also decreased P availability through the immobilization of P during the decomposition of its litter (Vitousek & Walker, 1989), and negatively affected the regeneration of the dominant native tree (Walker & Vitousek, 1991). Notably, despite increasing N availability and N emissions across a variety of Hawaiian ecosystems, *M. faya* invasion did not increase aboveground biomass at the landscape-scale, reflecting that other factors (e.g. losses of native understory species and low water availability) ultimately constrain the system's NPP (Asner *et al.*, 2009).

The alteration of stoichiometrically governed ecosystem feedbacks may thus further alter macro-scale biogeochemical fluxes by affecting plant and microbe community structure, including decomposer food webs (Moore *et al.*, 2005). Although individual soil organism populations might be expected to express a range of stoichiometric flexibility in response to environmental perturbation (Hall *et al.*, 2011), *in situ* stoichiometric studies of soil microbes are typically conducted at a higher community level of organization (Cleveland & Liptzin, 2007) and through the characterization of the processes which they regulate (e.g. soil respiration, extracellular enzyme-mediated decomposition).

Extracellular enzymes (which are produced primarily by microbes, although some are synthesized by plants) make nutrients and C available for uptake by catalyzing the breakdown of polymeric SOM (Allison *et al.*, 2010). The acquisition of nutrients thus requires an investment in N-rich extracellular enzymes, such that nutrient uptake is inherently coupled to nutrient loss (Marklein & Houlton, 2012; Mooshammer *et al.*, 2012). Organisms have developed strategies to minimize this system's inherent stoichiometric tradeoff in response to N or P limitation, which may feed back to ecosystem-scale processes. For example, a recent meta-analysis by Marklein & Houlton (2012) demonstrated that P-mineralizing phosphatase enzyme activity (from both plant roots and bulk soil) is increased by N fertilization in P-limited systems, whereas P fertilization strongly suppresses phosphatase activity. Further, the synthesis of extracellular enzymes appear to be regulated stoichiometrically, as the activity of enzymes targeting more P-, N- or C-rich compounds correlates with microbial demand (Sinsabaugh *et al.*, 2008).

Extracellular enzyme activity therefore links SOM decomposition with microbial community structure, driving a feedback between environmental conditions, plant and decomposer community dynamics. Changing soil conditions may also drive the microbial community towards a more fungal-like (higher microbial biomass C : N ratio) or more bacterial-like (lower C : N ratio) composition (Strickland & Rousk, 2010), which can significantly alter C and nutrient cycling dynamics. Greater fungal to bacterial dominance is often associated with lower N availability and increased oxidative enzyme activities, which tend to mediate the decomposition of recalcitrant soil compounds. By contrast, higher N availability tends to be correlated with increased hydrolytic enzyme activities, which are associated with the degradation of more labile compounds (Sinsabaugh *et al.*, 2008; Sinsabaugh, 2010). For example, in N-rich tropical

soils, N fertilization increases hydrolytic enzyme activity and accelerates the decomposition of the labile soil C pool, whilst concurrently decreasing oxidative enzyme activity and the decomposition of the more recalcitrant C pool (Cusack *et al.*, 2010).

If litter lability increases with invasion, warming or nutrient addition (Weintraub & Schimel, 2003; Allison & Vitousek, 2004; Sturm *et al.*, 2008) and decreases SOM C : N, the soil faunal composition may shift towards a more rapidly cycling, bacterial consumer-based community at the expense of the fungal community and their consumers. By contrast, if food web perturbations increase more recalcitrant, C-rich SOM litter inputs, such as lignified tissues (Weintraub & Schimel, 2005), a slower cycling, fungal-dominated community may be favored (Moore *et al.*, 2005). Fungal-based food webs may be more resistant (but less resilient) than bacterial-dominated communities to drought and similar climate perturbations because of these differences in their life history strategies (de Vries *et al.*, 2012). Alternatively, fungal-based food webs may be less resistant than bacterial-dominated communities to physical stressors, such as soil habitat fragmentation driven by land use change (Hedlund *et al.*, 2004). Therefore, shifting between bacterial and fungal dominance can have significant ramifications for both ecosystem nutrient cycling and subsequent responses to perturbation.

Numerous studies have suggested the potential for these types of feedbacks between aboveground and belowground communities in response to perturbation to further alter ecosystem stoichiometric relationships. Under both warming and fertilization, ectomycorrhizal biomass increased in a tundra ecosystem because these symbionts tracked the rise in shrub abundance, creating a positive feedback that further facilitated shrub growth (Clemmensen *et al.*, 2006; Deslippe & Simard, 2011). Similarly, eCO₂ can stimulate C inputs into the soil whilst reducing N availability, which may promote soil fungal abundance (Klamer *et al.*, 2002; Janus *et al.*, 2005; Lipson *et al.*, 2005; Carney *et al.*, 2007). For example, Carney *et al.* (2007) reported that eCO₂-driven increases in plant-derived soil inputs promoted the relative abundance of fungi and stimulated oxidative enzyme activity, offsetting nearly 52% (442 g C m^{-2}) of the additional C gained through increased NPP by a scrub-oak ecosystem.

Trophic interactions and disturbance

Complementing plant–decomposer stoichiometric feedbacks, plant anabolism and allocation of C and nutrients in response to perturbation may further alter the trajectory of net C storage by changing trophic interactions which can cascade through food webs. For example, eCO₂ can lower the quality of plant tissue (widening C : nutrient ratios), increasing the amount of tissue insect herbivores must eat to meet their metabolic demands (Stiling *et al.*, 1999). Similarly, chronic N deposition has been found to widen foliar N : P ratios and to intensify P limitation in insect herbivores (Elser *et al.*, 2000). Notably, although eCO₂ tends to reduce insect herbivore performance, these effects can be mitigated in combination with greater temperature by

stimulating herbivore browsing activity, whilst increasing the quality of plant leaf tissue, relative to eCO₂ alone (Zvereva & Kozlov, 2006). Stoichiometric feedbacks can also occur between primary producers and megafauna. In Arctic systems, for instance, the effects of warming on increased shrub production can be offset by greater muskoxen and caribou herbivory (Post & Pedersen, 2008; Olofsson *et al.*, 2009).

At the biome scale, plant community change may feed back with large-scale disturbance regimes. For example, tundra fires appear to have been more common under ancient birch-dominated conditions, because woody biomass created an abundance of fine fuels (Higuera *et al.*, 2008). Fire may drive significant ecosystem N and C loss because of their relatively low volatilization temperatures, whilst converting aboveground P into available mineral forms through ash deposition (Boerner, 1982). In tallgrass prairie soils, for instance, an experimental fire simulation promoted cyanobacteria N fixation as the available N relative to available P (aN : P) declined. This study yielded a maximal estimate of 21 kg N-fixed ha⁻¹ yr⁻¹ following fire lowering of aN : P (Eisele *et al.*, 1989); a fraction of which would offset a significant portion of the 18 kg N ha⁻¹ yr⁻¹ estimated to be lost via fire in ungrazed prairie systems (Hobbs *et al.*, 1991). Trophic cascades and disturbance feedbacks to stoichiometric change can thus ultimately regulate C accumulation and other macro-scale ecological processes, regardless of a system's potential stoichiometric flexibility.

Synthesis

Biological systems have long been recognized to use essential elements at characteristic ratios that differ systematically among molecules, tissues and organisms (Sterner & Elser, 2002). The flexibility of these relationships in response to global change stressors, however, remains an area that is ripe for exploration. A major challenge faced in the understanding of long-term ecological responses to environmental change is that outcomes based on short-term experimental manipulations may not accurately reflect long-term trajectories. The application of a stoichiometric approach to the evaluation of such studies might help to better constrain these projections by highlighting stoichiometric thresholds in which observed changes over the short term can realistically be expected to significantly influence macro-scale processes over time.

A consideration of the range of stoichiometric responses to perturbation relative to resource availability, ontological stage or community composition provokes additional questions.

- How much stoichiometric flexibility do systems have to maintain macro-scale processes (e.g. C sequestration) without undergoing a shift to a new state (e.g. a transition from grassland to shrubland)?
- How is the potential range of stoichiometric flexibility related to the relative nutrient richness of a system?

These uncertainties highlight the fact that the potential for lagged responses, areas for local stability and thresholds to stoichiometric change must be addressed in concert with the identification of stoichiometric flexibility. As such, researchers

should bear in mind that empirical studies serve as snapshots in time and space of dynamic processes in systems under change. Therefore, a coupled measurement–model approach (Conant *et al.*, 2011) represents a particularly powerful method to explore stoichiometric flexibility phenomena over multiple scales.

Notably, stoichiometric constraints are one of many factors that influence community structure and ecosystem processes (Moe *et al.*, 2005). As such, the range of elemental ratios alone can serve as boundary conditions. However, changes in substrate use and synthesis efficiency will reflect both the variation in chemical structure and elemental ratios (Elser *et al.*, 2010), and may control where within these boundaries a system functions. Similarly, abiotic factors linking elements to biota – such as hydrological connectivity – will be key regulators in the potential for stoichiometric response to perturbation. Nevertheless, framing global change questions within a stoichiometric flexibility framework may help to guide the understanding of controls on the variability of ecosystem responses to perturbation.

Although potential stoichiometric range tends to decrease with increasing scale, the transition from the expression of stoichiometric plasticity within organisms to the community and ecosystem scales appears to be a key threshold when considering its impact on ecosystem processes in response to perturbation. Thus, the identification of the mechanisms controlling the linkages between the individual-, community- and ecosystem-level expression of stoichiometric flexibility is particularly relevant when applying a stoichiometric framework to global change problems. Within the biologically defined boundaries on the physiological plasticity of organisms, shifting resource limitation appears to be a primary constraint on the expression of stoichiometric flexibility at the organismal scale for both primary producers and their consumers. In contrast, by assuming maximum expression of the stoichiometric range of organisms, stoichiometric flexibility from the community to ecosystem scale is likely to be ultimately regulated

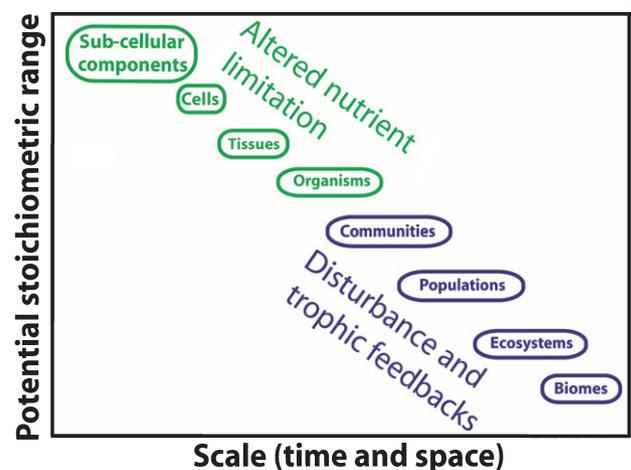


Fig. 2 Conceptual diagram of the stoichiometric range potential of nested biological states that are linked across increasing scale. At smaller levels of biological organization (green), a change in nutrient limitation is likely to be a primary regulator of the expression of stoichiometric flexibility within the potential range. At larger scales (blue), disturbance dynamics and trophic feedbacks are major regulators of the expression of stoichiometric flexibility.

by disturbance dynamics and trophic feedbacks (Fig. 2). Therefore, the duration and magnitude of altered C and nutrient cycling dynamics in terrestrial systems under change will be regulated by both the stoichiometric plasticity of their organisms and the large-scale controls on the ecosystems that they build.

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