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Nitrogen and Nature

Anthropogenic changes to the global N cycle are important in part because added N alters the composition, productivity, and other properties of many natural ecosystems substantially. Why does added N have such a large impact? Why is N in short supply in so many natural ecosystems? Processes that slow the cycling of N relative to other elements and processes that control ecosystem-level inputs and outputs of N could cause N supply to limit the dynamics of ecosystems. We discuss stoichiometric differences between terrestrial plants and other organisms, the abundance of protein-precipitating plant defenses, and the nature of the C–N bond in soil organic matter as factors that can slow N cycling. For inputs, the energetic costs of N fixation and their consequences, the supply of nutrients other than N, and preferential grazing on N-fixers all could constrain the abundance and/or activity of biological N-fixers. Together these processes drive and sustain N limitation in many natural terrestrial ecosystems.

INTRODUCTION

Human alteration of the N cycle is important in large part because added N has myriad effects on nontarget ecosystems (1). Enrichment with N often affects the species composition, productivity, dynamics, and diversity of recipient ecosystems (2, 3). Increased plant growth in response to N additions has been documented well in a broad range of systems (4, 5). The growth of many animals, indeed the health of much of humanity, is constrained more by protein supply than by energy (6), and decomposition and other microbial processes can be shaped substantially by the supply of available N.

Our purpose in this paper is to address the question—'why is N so important to the functioning of ecosystems?' What processes cause N to be in short supply in many terrestrial ecosystems? It is no mystery why N limits production and yield in intensive agricultural systems—they are designed to maximize the removal of protein N for human or animal consumption, and they are disturbed frequently by tillage and harvest, allowing loss of N to streams, groundwater, and the atmosphere. Moreover, the species composition of agricultural systems is controlled, and unless they are managed for symbiotic N-fixers, such fixers are actively excluded. The combination of substantial N losses and very low rates of N fixation ensures that N is in short supply in agricultural systems (absent fertilization), and this combination entrains the high rates of N addition that intensive agriculture, and our population and civilization, depend upon.

Natural ecosystems differ fundamentally from intensive agricultural systems. First, the lack of harvest and relatively infrequent disturbance mean that N and other elements can accumulate from season to season, eventually building up a pool of available N within the system. Second, N fixers can colonize and grow in such sites, and potentially can make up a deficit in the supply of N. Indeed, where plants with N-fixing symbioses dominate terrestrial ecosystems, they are capable of adding enough N to overwhelm almost any rates of N loss. Why then does N supply continue to limit the functioning of many natural ecosystems?

On short time scales, the relative rates at which elements cycle within ecosystems determine their relative availability, and hence the likelihood of limitation by particular elements. On long time scales, the balance between inputs and outputs determines the quantity of each element in circulation, and so the likelihood of limitation. Here, we ask if there are features of the N cycle that make limitation by N more likely than limitation by other nutrients, in the absence of substantial inputs of N *via* fixation. We then evaluate processes that could enhance or retard losses of N from ecosystems, relative to those of other elements. Finally, we evaluate processes that could constrain rates of biological N fixation, even where N is in short supply.

N CYCLING

We identify 3 types of processes that could slow cycling of N relative to at least some other elements: *i*) the stoichiometry of different groups of organisms within ecosystems; *ii*) the widespread occurrence of protein-precipitating compounds in plants and soils; and *iii*) the nature of the C–N bond in litter and soil organic matter.

Stoichiometry

Organisms use essential elements at characteristic ratios, and these ratios differ systematically among different groups of organisms (7). Element ratios are widely used in the analysis of marine ecosystems (8, 9). Their application is usually less explicit in terrestrial ecology, but they provide the basis for using critical element ratios to predict element mineralization or immobilization during decomposition. One general feature of terrestrial ecosystems is that C:element ratios in plants, especially trees, are much wider than those in other organisms as a consequence of plants' use of C-based compounds (cellulose, lignin) to provide structure. For N in particular, soil bacteria generally have a C:N ratio near 6, while plants often have C:N ratios > 100. Even the leaf litter produced in forests on infertile soils can have C:N ratios in excess of 100 (10).

Consequently, relative to their own requirements, animals and microbes live in a C-rich, N-poor world. Animal nutrition and growth are often constrained by the N content of their food, and protein deficiency is widespread (6). This difference in stoichiometry can sustain N limitation to animals even where plants are not limited by N supply. Microbes also encounter little N (relative to their requirements) in the plant litter they decompose, and so they retain the N they obtain from their substrate and acquire more directly from inorganic pools in the soil. As a result, N cycling from organic matter back to biologically available forms lags behind the decomposition of plant litter.

Protein-precipitating Defense

Terrestrial plants are long-lived relative to most of their herbivores, and so plant tissues are exposed to those herbivores for extended periods of time. Given the apparent vulnerability of plants to herbivores, why are most plant tissues, especially those in forests, not largely consumed by herbivores? Why is the world green? (11, 12).

Stoichiometric differences between plants and animals could slow the growth of herbivores systematically. Perhaps more im-

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portantly, plant tissues are defended chemically against herbivores (13). Defensive compounds include a broad array of chemicals with differing modes of action, but one of the most important and widespread classes is protein-precipitating phenolic compounds. When plant tissue is consumed, these compounds are released from vacuoles or cell walls, oxidized, and can bind with plant proteins and herbivore digestive enzymes (14, 15). Polyphenols can thereby prevent an herbivore from deriving much benefit from the plant. While other defensive compounds (e.g. alkaloids and terpenes) are more toxic, the evolution of detoxifying pathways in herbivores can overcome their effects. In contrast, countermeasures to the mode of action of protein-precipitating defenses have not evolved. Protein-precipitating defenses are present at high concentrations in many plants, especially those growing on infertile soils—up to 20% of dry mass for polyphenols in leaves, more than 30% for lignin (16). While the C-rich stoichiometry of terrestrial plants affects all elements, protein-precipitating defenses affect N assimilation in particular, and may be largely responsible for making N limiting to the growth of many herbivores.

The abundance of protein-precipitating compounds in plants may be selected based on their role in defense against herbivores, but their significance extends beyond defense (17). It has long been recognized that the same compounds that inhibit herbivory also can slow rates of decomposition (18, 19) and inhibit microbial activity (20). The input of soluble polyphenols from plant litter into the soil can be up to 5% of net primary production. Soluble polyphenols disappear quickly from decomposing plant litter, reaching undetectable levels within litter soil after just a few weeks of decomposition (21). Because most polyphenols are relatively recalcitrant to microbes, the majority are not likely to be decomposed in this short period of time, but rather "hidden" from detection in organic complexes.

Lignin and microbial cell walls also contribute recalcitrant phenolic compounds to soil. During decomposition, these aromatic compounds can be oxidized to form reactive free radicals that can then polymerize and trap N-containing compounds (e.g. ammonium and amino acids) in humic complexes (22, 23). While P and other elements can also be found in humic compounds, the physiochemical properties of N (electron configuration, bond formation) allow it to form extremely recalcitrant associations with carbon, slowing the cycling of N relative to other elements.

The Carbon-Nitrogen Bond

Most organic N is covalently bonded to C (–C–N–). In contrast, much organic S and most organic P is covalently bonded to oxygen rather than C, forming an ester bond (–C–O–S or –C–O–P) (24, 25). Most other elements associated with organic matter (e.g. Fe, Mg, Ca, K, etc.) are ionically bonded or loosely coordinated with organic compounds.

These differences in how nutrients are held in organic matter can control the relative rates at which elements cycle within ecosystems. As described above, organic N often is bound up by protein-precipitating compounds and combined with recalcitrant C compounds. The N in these compounds is chemically as well as physically protected. In contrast, P-containing groups are highly charged, preventing their entrainment in strongly humified materials and confining them to the reactive side chains of organic matter (26). These accessible reactive phosphates can adsorb to soil minerals or be released from the organic matter. Sulfate esters behave in a similar manner.

Because of these differences in binding and stabilization within soils, mineralization of N is much more complicated, costly, and thus slower than is mineralization of other elements. The release of N from organic compounds and humic complexes requires the coordinated action of several enzymes. Since N is a fundamental constituent of all enzymes, it may not be rewarding for biota to spend N to build enzymes in order to acquire more N. Often the release of N is coupled to decomposition of organic matter, and microbial demand for C as an energy source rather than demand for N can control the release of N (24).

In contrast, exposed ester P or S linkages are readily cleaved in a single step by extracellular phosphatase or sulfatase enzymes that can be produced by roots, mycorrhizae, and soil microorganisms (27, 28). When P is in short supply, spending N to build enzymes that acquire P can be rewarding. N additions have been shown to stimulate phosphatase production in a range of ecosystems (29–31). Phosphatases in particular are inducible, being synthesized in greater quantities when P is in short supply (32). Overall, P mineralization can be responsive to P demand within ecosystems.

Mineralization of P and S esters cannot be controlled completely by P or S demand. Decomposition of structural material in litter may be required before extracellular enzymes can gain access to the ester-containing compounds (33). Nevertheless, P and S cycling are relatively more flexible than N cycling in most ecosystems. Where decomposition is slow, as in cold, dry, or infertile sites, N mineralization also is slow. In contrast, P mineralization can "run ahead" of decomposition in ecosystems where P is in short supply.

INPUT-OUTPUT BUDGETS

On long time scales, elements with ecosystem-level inputs less than outputs will decrease in abundance within ecosystems, and these elements are likely to come to constrain biological activity. With the exception of biological N fixation, which is discussed in the next section, are there systematic differences in element inputs and/or outputs between N and other elements that could drive ecosystems towards limitation by N?

Inputs

In the absence of N fixation, N is mostly derived from the atmospheric deposition of fixed N, which in turn is derived from trace-gas emissions upwind (or from lightning). In the absence of anthropogenic sources of N, such inputs generally are low (1, 34), although natural fires and even volcanic activity can supply large quantities of fixed N episodically (35, 36). In contrast, P and most other essential elements can be supplied by weathering of soil and rock. Where weatherable minerals exist in the rooting zone of ecosystems, inputs of these elements are relatively large. Inputs of P and cations fall to levels that can be less (relatively) than atmospheric N deposition in unpolluted regions only when weatherable minerals have become depleted, as occurs in many old tropical soils (37), or covered by thick organic layers. Consequently, ecosystems developing on new substrates have little N to start with, and they are likely to accumulate N slowly (in the absence of biological N fixation).

Outputs

As a monovalent anion, nitrate is more mobile in soils with net cation exchange than are cations and it is far more mobile than phosphate, which is subject to strong adsorption reactions as described above. Moreover, N also is subject to multiple pathways of gaseous loss; as ammonia in pH-dependent equilibrium with soil ammonium (38), as trace gases produced during nitrification and denitrification (39), and as dinitrogen produced when nitrate serves as a terminal electron acceptor in anaerobic metabolism. In contrast, most other essential elements nearly or wholly lack a gas phase.

Most pathways of N loss originate in biologically available forms of N, particularly nitrate. Most losses may therefore be

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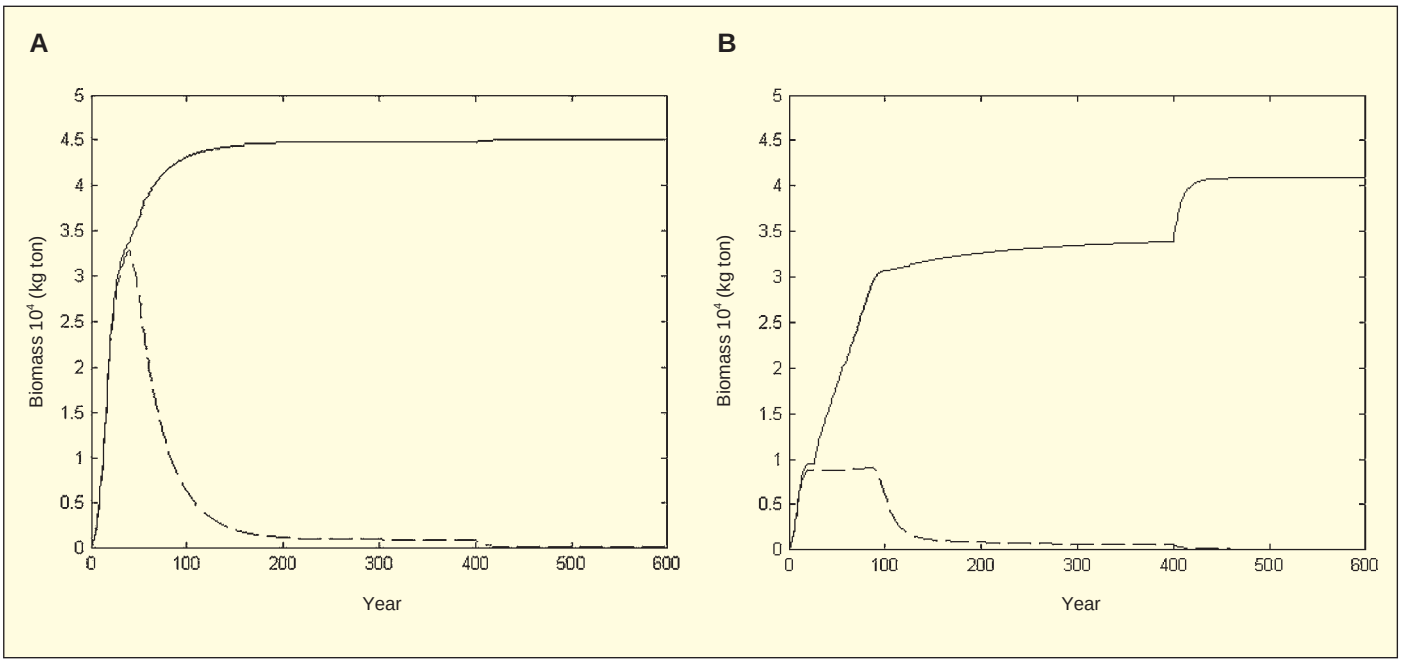

Figure 1. Simulated effects of constraints to symbiotic N fixation on total plant biomass (solid line) and the biomass of N fixers (dashed line).
A. Biomass assuming that symbiotic N fixation involves a substantial energy cost, but no additional constraints.
B. Biomass assuming that symbiotic N fixation is further constrained by differential shade intolerance, P limitation, and grazing.
In both cases, a step increase in N additions occurs in year 400; the magnitude of response to that addition is a measure of N limitation.
Based on analyses in Vitousek and Field (51).

'controllable' biologically if nitrate pools in soil are small, as they should be, where N supply is limiting to biological activity. Consequently, the potential for rapid losses of N may not be realized fully in practice. However, spatial and temporal variations in the balance between N supply *vs* demand can allow the accumulation and loss of available forms of N, even within ecosystems where N supply generally limits biological activity (40, 41). Moreover, dissolved organic N (DON) may represent a pathway of loss that is largely independent of N availability (42–44). Where such losses are large (relative to N inputs), they can constrain ecosystem-level N accumulation and sustain N limitation. While dissolved organic forms of P (DOP) and other elements also can be lost, P can be retained relative to C and N by the systematic removal of P from dissolved organic matter as it leaches through forest ecosystems (45, Hedin et al. unpubl.), probably by the activity of extracellular phosphatases.

In the absence of N fixation, the limited sources of N, and its mobility relative to other elements, could drive ecosystems towards limitation by N, particularly in sites that are geologically young enough to contain weatherable minerals within the rooting zone. Most temperate and boreal ecosystems should fall in this category, because most of these systems have been affected repeatedly by glaciation.

BIOLOGICAL N FIXATION

Although many of the processes discussed above could drive terrestrial ecosystems towards limitation by N, biological N fixation has the capacity to add enough N to overwhelm slow N cycling and/or substantial N losses, and the capacity to fix N is widely distributed both taxonomically and geographically (46). Moreover, N-fixers should have a competitive advantage where N supply is deficient, and as a by-product of their activity N-fixers should drive an increase in inputs; where N is in excess, fixers would have no advantage, and fixation should cease. Biological N fixation could thereby regulate N availability. Just that occurs in temperate lakes (47); why not in most or all ecosystems?

A number of reasons why N fixation could fail to respond to N deficiency were summarized in a recent review (48); these are discussed briefly here. The energetic cost of N fixation is one reason: depending on the organism, N fixation requires the construction of specialized structures and protection against oxygen as well as incurring the direct cost of reducing dinitrogen (49). However, the direct cost of fixation is not much greater than that of nitrate reduction (50), and modeling studies of symbiotic N-fixers suggest that energetics alone are insufficient to cause more than marginal limitation by N (52).

Several recent models have investigated why biological N fixation fails to respond to ecosystem-level N deficiency, for organisms from vascular plants with rhizobial and actinorrhizal symbioses (51, 52), through cyanobacteria in estuaries (53), to heterotrophic bacteria involved in litter decomposition (49). For symbiotic N-fixers, processes that could constrain biological N fixation include a relatively greater shade intolerance by N-fixers (51); limitation by P or other nutrients, due to a greater demand for these elements by N-fixers (54, 55, see also 56); and grazing on the relatively protein-rich tissues of N-fixers (57–59). Model results suggest that in combination, these processes could suppress N fixation sufficiently to sustain substantial N limitation indefinitely (51) (Fig. 1).

In cyanobacterial systems, a low supply of P (or high N:P ratios) can suppress N fixation on land (60, 61) as it does in lakes. In estuaries, Howarth et al. (53) modeled constraints to N fixation and found that an interaction of trace metal limitation (Mo was modeled, but Fe could be at least equally important) and grazing sufficed to suppress N-fixers and sustain N limitation. A greater turbulence in estuaries compared to lakes could also break up cyanobacterial aggregates and suppress N fixation (62).

For heterotrophic bacteria, an experimental study in the Hawaiian Islands showed that the C quality of plant litter ultimately constrained rates of N fixation during litter decomposition. Heterotrophic N fixation was substantial during the decomposition of high quality (low lignin) litter, and the decomposition rate of that litter was enhanced by experimental N additions (63, 64). In contrast, low quality litter with high lignin concentrations was

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produced in nutrient-limited forests. Very little N was fixed as this litter decomposed, and added N had little effect on its rate of decomposition (Fig 2). This disconnect between plants (which are limited by N and produce low quality litter) and microbes (which are limited by low C quality rather than N, and so do not fix N) could be important to maintaining ecosystem-level N limitation (64).

There are several common features to the controls of N-fixing systems that have been evaluated to date. For example, elements other than N can be important in constraining N fixation; what appears to be N limitation in some systems may be limitation by P (or another element) in disguise. Similarly, grazing on protein-rich or otherwise vulnerable N-fixers can selectively remove them from communities on land and in estuaries.

CONCLUSIONS

Because N supply often limits primary production and other ecosystem processes over much of the natural world, human alteration of the N cycle has the capacity to change Earth's ecosystems substantially (1–3). Why is N limitation so widespread? A number of factors within ecosystems, including contrasts in tissue stoichiometry between terrestrial plants and their grazers and decomposers, the widespread distribution of protein-precipitating defensive compounds, and the nature of the C–N bond in litter and soil organic matter, can combine to make N cycle more slowly through terrestrial ecosystems than other biologically essential elements. Moreover, N is more readily lost from ecosystems to streamwater, groundwater, and the atmosphere than are most other essential elements—so N losses can also drive ecosystems towards N limitation. Most importantly, a number of additional factors, including energy constraints, limitation by nutrients other than N, and grazing, can reduce rates of biological N fixation in ecosystems substantially, even where N limits primary production and other ecosystem processes. A serious effort to identify and determine the relative importance of these processes, and how they may be affected by other components of anthropogenic global change, would likely prove rewarding.

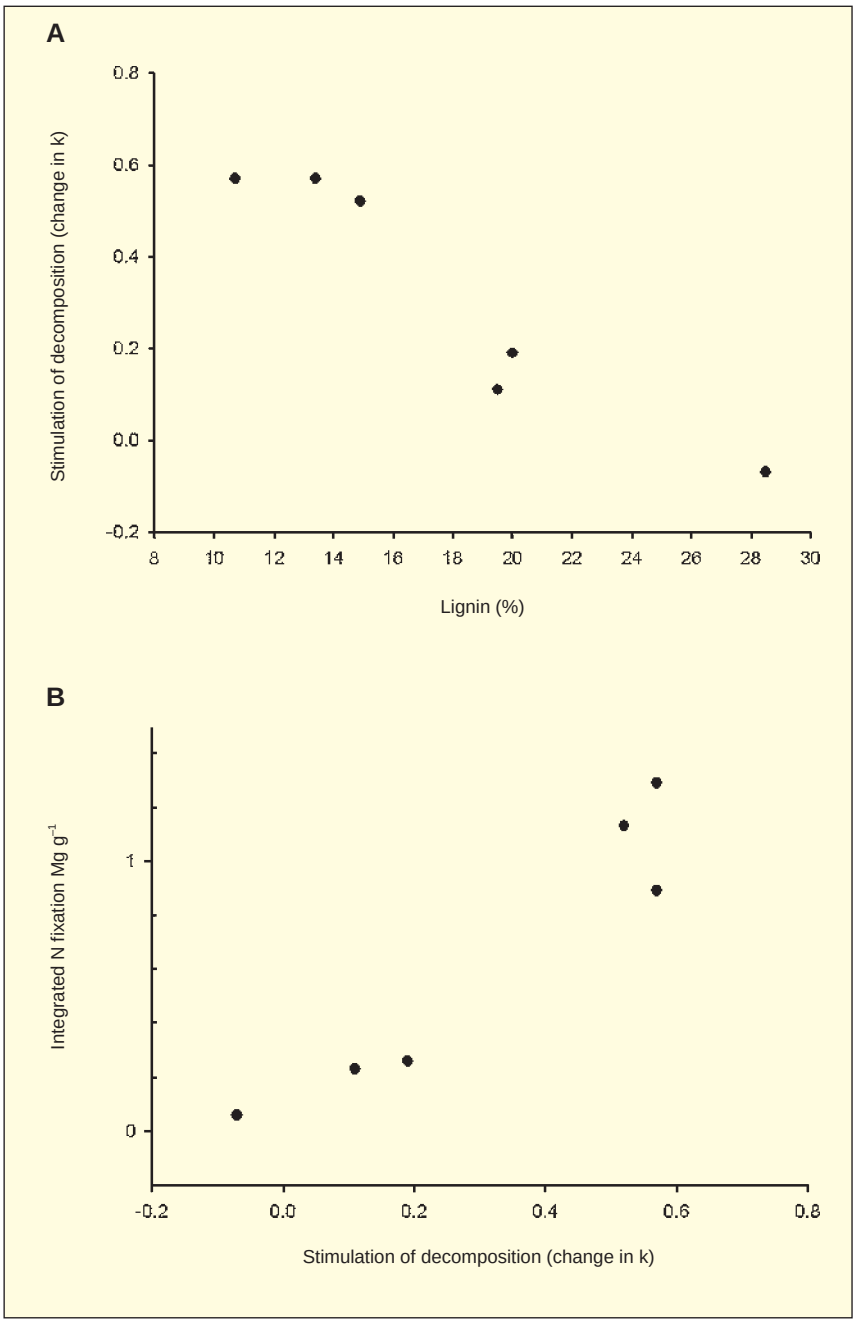

Figure 2. A. The relationship between lignin concentration (a measure of carbon quality) and the increase in decomposition rate caused by added N in *Metrosideros polymorpha* litter from Hawaii. From Hobbie (63, 65).
B. Relationship between the increase in decomposition rate caused by added N (a direct measure of N limitation to decomposition), and the integrated quantity of N fixed during the decomposition of unamended *Metrosideros* litter. From Vitousek and Hobbie (64).

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