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Nitrogen deposition: A component of global change analyses

Short title: *Nitrogen deposition and global change*

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SUMMARY

The global cycles of carbon and nitrogen are being perturbed by human activities that increase the transfer from large pools of nonreactive forms of the elements to reactive forms that are essential to the functioning of the terrestrial biosphere. The cycles are closely linked at all scales, and global change analyses must consider carbon and nitrogen cycles together. The increasing amount of nitrogen originating from fossil fuel combustion and deposited to terrestrial ecosystems as nitrogen oxides could increase the capacity of ecosystems to sequester carbon, thereby removing some of the excess carbon dioxide from the atmosphere and slowing the development of greenhouse warming. Several global and ecosystem models have calculated the amount of carbon sequestration that can be attributed to nitrogen deposition, based on assumptions about the allocation of nitrogen among ecosystem components with different carbon:nitrogen ratios. They support the premise that nitrogen deposition is responsible for a an increasing terrestrial carbon sink since industrialization began, but there are large

uncertainties related to the continued capacity of ecosystems to retain exogenous nitrogen. Whether terrestrial ecosystems continue to sequester additional carbon will depend in part on their response to increasing atmospheric carbon dioxide concentrations, which is widely thought to be constrained by limited nitrogen availability. Ecosystem models generally support the conclusion that the responses of ecosystems to increasing concentrations of carbon dioxide will be larger, and the range of possible responses will be wider, in ecosystems with increased nitrogen inputs originating as atmospheric deposition. The interactions between nitrogen deposition and increasing carbon dioxide concentrations could be altered considerably, however, by additional factors, including nitrogen saturation of ecosystems, changes in community composition, and climate change. Nitrogen deposition is also linked to global change issues through the volatile losses of nitrous oxide, which is a potent greenhouse gas, and the role of nitrogen oxides in the production of tropospheric ozone, which could interact with plant responses to elevated carbon dioxide. Any consideration of the role of nitrogen deposition in global change issues must also balance the projected responses against the serious detrimental impact of excess nitrogen on the environment.

Key words: atmospheric carbon dioxide, C:N ratio, global carbon cycle, global change, nitrogen deposition

INTRODUCTION

Global stocks of both carbon (C) and nitrogen (N) can be characterized by large, nonreactive pools from which a small portion is converted to a reactive form and then rapidly converted back to the nonreactive pool (Schlesinger, 1991). While the C and N atoms are in reactive compounds, they

circulate, combine, and interact in myriad ways. Although the amount of these reactive C and N compounds comprise but a tiny fraction of the total stocks, and their lifetime is a tiny fraction of the turnover time of the larger pools, these fluxes support all life on our planet. Hence, the fluxes into and out of these reactive C and N pools, and the interactions they undergo while they are in a reactive state, are what we really care about. Imbalances in the transfer to and from the reactive pools—seemingly trivial and certainly undetectable relative to the total size of the C and N stocks—can make overwhelming differences to our quality of life. Human intervention in the transfer from nonreactive to reactive pools has created imbalances, and the consequences are of the greatest concern. This is particularly so with regard to the combustion of fossil fuels. Nonreactive C and N are oxidized, releasing carbon dioxide (CO_2) and nitrogen oxides (NO_x = NO + NO_2) into the atmosphere and converting additional dinitrogen gas (N_2) into NO_x in the process. After additional transformations in the atmosphere, nitrogen oxides are collectively referred to as NO_y (= NO_x + any single N species with an oxygen atom; Galloway *et al.*, 1995).

Because this anthropogenic release of CO_2 and NO_x are linked at the source, and because they interact so completely while they circulate in their reactive forms, the imbalances in C and N fluxes cannot be analyzed separately. The metabolism and cycling of C and N are closely linked at the scale of an individual chloroplast or leaf as well as at the whole-plant or ecosystem scales. However, there are enough differences in the deposition characteristics of C and N to make it difficult to analyze them together. Carbon dioxide has a much longer residence time in the atmosphere than the more reactive NO_y compounds. Hence, CO_2 is generally evenly distributed throughout the atmosphere, whereas the more reactive NO_y (as well as ammonium gases and particles, collectively called NH_x) are usually deposited relatively close to the source, often dissolved in precipitation, but also being absorbed by plants directly in a gaseous form. The chemistry of NO_y creates much greater spatial heterogeneity in

its deposition than that for CO_2; hence, the interactions between CO_2 and NO_y can be difficult to predict. But given the prominent influence of terrestrial ecosystems on the global carbon cycle, the terrestrial nitrogen cycle and its perturbation by deposition of anthropogenically derived nitrogen oxides will have ramifications through the global C cycle and the climate system. Despite the difficulties, N deposition must be considered in relation to other aspects of global change.

In this paper three primary questions will be explored. Does N deposition lead to additional removal and storage of fossil-fuel derived C from the atmosphere? Will N deposition influence the response of plants and ecosystems to the higher concentrations of CO_2 in the atmosphere of the next century? Do higher CO_2 concentrations and N depositions alter the volatilization and release of N from ecosystems? There are a number of secondary issues to consider as well, including the interaction of CO_2 and tropospheric ozone, species replacement, and the influence of other changing environmental factors.

NITROGEN DEPOSITION AND THE MISSING CARBON SINK

Global carbon cycle

A great deal of research in the global change arena has been focused on the problem of the "missing C sink". The missing sink, usually estimated to be < 2 Pg yr^{-1} (1 Pg = 10^{15} g)(Schimel, 1995), is the amount of C that is emitted to the atmosphere by human activities—fossil fuel combustion, cement manufacturing, and deforestation—that cannot be accounted for as an accumulation in the atmosphere or the modeled net flux of C into the ocean. There is a presumption that the missing sink resides in the terrestrial biosphere, a premise that is supported indirectly through measurements of the seasonal oscillations and latitudinal distribution of atmospheric CO_2 (Tans, Fung & Takahashi, 1990). But direct observations of terrestrial C pools and fluxes cannot hope to find a net flux of 2 Pg yr^{-1} into a

terrestrial C pool that is about 2200 Pg, with annual gross fluxes in and out of about 60 Pg (Schimel, 1995). Instead, we rely on models of terrestrial ecosystems that try to capture the important elements of C cycling, and our understanding of how those cycles might be perturbed, to calculate the "missing" C (VEMAP Members, 1995). Two questions must be asked: can we account for the C that has been emitted since industrialization began, and how will C fluxes change over the next century as we continue to burn fossil fuels? The answer to the first question, which is constrained by the historical record of emissions and atmospheric CO_2 concentrations, should provide guidance for answering the second question, which is constrained only by scenarios of fossil fuel use and our general understanding of how our planet works. Clearly the second question will always be fraught with uncertainty, but changes in the global C cycle and the resultant concentration of CO_2 in the atmosphere are the major drivers of climate change, so the difficult questions cannot be ignored.

From a general understanding of the important controllers of ecosystem production and C storage comes the premise that, on a global scale, the only processes that could sufficiently stimulate terrestrial biosphere productivity are fertilization with increasing atmospheric CO_2 concentrations, fertilization by N, or increasing land cover (Schimel, 1995). The potential role of N fertilization seems clear: the productivity of many natural ecosystems worldwide is limited by the lack of available N (Vitousek & Howarth, 1991). Experimental fertilization of forests with N has demonstrated their capacity to respond with greater productivity (Johnson, 1992), and productivity is generally higher on sites with greater N availability (Pastor *et al.*, 1984). Agricultural productivity over the last century has increased sufficiently to feed an exponentially growing population only because of human intervention in the N cycle through the industrial production of ammonia fertilizer and the cultivation of legumes (Smil, 1997). But agriculture is only a small fraction of the terrestrial C budget, and forests, which dominate the C budget, are rarely fertilized (deliberately) on a large scale.

The inadvertent fertilization of forests and other N-limited ecosystems with N deposition from the atmosphere can, therefore, be expected to increase productivity over that in pre-industrial times. In the absence of human activities, N was transferred from the huge pool of nonreactive atmospheric N_2 to reactive forms (NO_y and NH_x) only through biological N_2 fixation and (to a much smaller extent) lightning (Galloway *et al.*, 1995). Most of the reactive N that formed in terrestrial systems was retained, but it was balanced by an approximately equal flux of reactive N back to nonreactive N_2 and N_2O by denitrification, so N did not accumulate. With industrialization came a large increase in the conversion of N to reactive forms through fossil fuel burning, fertilizer production, and legume cultivation. Much of this anthropogenic N is redistributed through waters or through the air (Galloway *et al.*, 1995), and thereby can be deposited onto forests.

Modeling approaches

The first attempt at estimating the amount of C storage that could be attributed to N deposition came from Melillo & Gosz (1983). Starting with a fossil fuel emission rate of 24 Tg N yr^{-1} (1 Tg = 10^{12} g) they assumed that 25%, or 6 Tg yr^{-1}, was distributed over forests. If all of this N combined with C in vegetation with a C:N ratio of 150, then 0.9 Pg C would be stored as a result of the fossil fuel N. However, not all of the N deposited on a forest is retained, and not all of the retained N ends up in vegetation. Melillo & Gosz assumed an average retention of 60%, and they distributed the N according to the initial distribution of C between vegetation, litter, and soils for different forest ecosystems, reducing their estimate to about 0.3 Pg yr^{-1}. This amount was considered to be the *maximum* amount of C that could be stored as a result of N deposition. Peterson & Melillo (1985) modified that estimate by distributing the N to different ecosystem pools based on the initial N distribution rather than the initial C distribution, thereby keeping C:N ratios constant. This change

lowered the C storage in forests to about 0.1 Pg yr^{-1}, and an additional 0.09 Pg yr^{-1} was associated with N loading in coastal zones and the open ocean.

These estimates of C storage stimulated by N deposition are much lower than more recent estimates, primarily because the amount of anthropogenic N deposition is now understood to be much higher. Galloway *et al.* (1995) estimate that human activity produces about 140 Tg of reactive N through energy production (21 Tg), fertilizer production (79 Tg), and legume and rice cultivation (40 Tg). About 55% of this is emitted to the atmosphere, and 70 to 80% of the atmospheric emissions are redeposited to terrestrial ecosystems. Hence, the 22 Tg N deposited to terrestrial ecosystems annually as NO_y is almost 4-fold higher than the 6 Tg assumed by Peterson & Melillo (1985). The difference can be attributed to a better knowledge of the gaseous emissions of reactive N from fertilized soil and biomass burning, as well as newer estimates of the distribution of N deposition around the globe.

Field *et al.* (1992) used a similar approach to that of Peterson & Melillo (1985) but with more recent deposition data. Starting with an N deposition (wet and dry) of 25 Tg yr^{-1} to temperate and boreal regions of the northern hemisphere, they assumed half of that amount enters N-limited systems. Their estimates for the associated C storage ranged from 2.5 Pg yr^{-1} if all of the N was incorporated into wood with a C:N ratio of 200, to 0.3 Pg yr^{-1} if all of the N was incorporated into humus with a C:N of 12. They suggested the lower value to be more likely.

Schindler & Bayley (1993) assumed an N deposition rate of 64 Tg yr^{-1}, 13 Tg of which is deposited on land. Multiplying this by an average ecosystem C:N ratio of 50, 100 or 150, they calculated the resulting terrestrial C storage to range from 0.65 to 1.95 Pg yr^{-1}, with an additional 0.36 Pg C taken up in oceans (C:N ratio = 7). Hence, of the increase in C stimulated by N fertilization, 64 to 84% was accounted for by the terrestrial biosphere. They assumed that this N-driven C sink probably developed largely in aggrading European and eastern North American forests within the past

century. They also noted that the calculations are very difficult because of the diversity of ecosystem types, C:N ratios and turnover time of different C and N pools, as well as uncertainty in deposition rates (especially dry deposition) and retention efficiencies of different ecosystems. They did not include the effect of the application of N fertilizer to agricultural soil.

Townsend *et al.* (1996) estimated the patterns of terrestrial C storage due to N deposition in much the same way, but with much more detail on the partitioning of N between different pools within an ecosystem and the distribution of N deposition to different ecosystems. They considered only fossil fuel N, because it is the largest source of oxidized N added to the atmosphere, and it is the only source for which there are good data on temporal trends. Atmospheric NH_x is primarily of agricultural origin, so they assumed that much of the deposition would fall back onto agricultural areas. Actually, inputs of NH_x to forests in eastern United States and Europe can be substantial, albeit less than NO_y inputs (Nihlgård, 1985; Lindberg *et al.*, 1986). Crop lands were not considered in the analysis because cultivation causes soil C to decline with time, crops have low C:N ratios and are harvested and consumed, and they already receive lots of N from fertilizer and N_2-fixing crops and so should be much less likely to respond to additional N deposition. Nitrogen oxide emissions from biomass burning are important globally (Galloway *et al.*, 1995), but they occur mostly in the tropics where N limitations are less common (Townsend *et al.*, 1996).

Townsend *et al.* (1996) calculated C storage using the CENTURY model. Carbon allocation to wood was fixed at 50% and C:N ratios were used for wood, non-wood, and three different soil pools. The geographic distribution of different biome types was interfaced with the modeled spatial distribution and temporal trend for NO_y deposition. Assuming that a constant 20% of available N was lost through leaching or volatilization, N-stimulated C uptake in 1990 was 0.74 Pg, and cumulative C storage since 1845 was 23.7 Pg. Nitrogen retention actually varies with vegetation type, forest age,

wet *vs.* dry deposition, and soil properties, and retention declines as a system reaches saturation. When losses in the model were increased linearly from 20% to 100% in low to high deposition areas, the estimate of the C sink was reduced by 40% (to 0.44 Pg yr^{-1} in 1990 and 18.5 Pg since 1845). This estimate represents about 25% of the missing C sink of 1.5 to 2 Pg yr^{-1}.

The C sink in the model was dominated by C storage in wood due to the high C:N ratio and long turnover time of wood (Townsend *et al.*, 1996). Conversely, C storage in soil was low because of its low C:N ratios, and only a small fraction of net primary productivity enters the soil organic matter pools. The C sink in this model was primarily in the north temperate region, between 25 and 55 degrees latitude; similar to the prediction of Tans *et al.* (1990). The most important areas for C storage were eastern U.S. and Europe, and to a lesser extent eastern Asia. These regions have both high NO_y deposition and extensive forested regions. The shorter turnover time of the non-woody vegetation in grasslands limits the C storage response to N deposition even when deposition is high.

The estimate of the N-stimulated C sink increased when all sources of N were included in the analysis. Holland *et al.* (1997) used three-dimensional chemical transport models to evaluate the importance of the spatial distribution of N deposition and to improve the quantification of the magnitude and uncertainty of N deposition. In addition to the fossil sources of NO_x included in other assessments, Holland *et al.* (1997) also included NO_y emitted from soils and biomass burning and NH_x from animal, soil, fertilizer, and biomass burning. Their estimate of the associated C sink was 1.5 to 2.0 Pg yr^{-1}, with 0.5 to 0.8 Pg yr^{-1} of that total attributable to NH_x.

These approaches all depend on C:N ratios for calculating C storage associated with a given level of N input. However, the stoichiometry of a terrestrial ecosystem, especially of a forest, is a much more difficult concept than the predictable stoichiometry of phytoplankton and bacteria that regulates element cycling in marine systems (Redfield, 1958). Because of the large amount of C-containing

structural tissue, the occurrence of storage of N in inactive forms, and the diversity of metabolic pathways in trees that alter C:N ratios, no single C:N ratio can be applied to all forests (Vitousek *et al.*, 1988). The use of C:N ratios in the modeling approaches can be best understood as a convenient way of incorporating allocation differences between ecosystems or in response to a perturbation rather than as the controlling mechanism of response. Townsend *et al.* (1996) point out that the simulations are likely to be more sensitive to changes in allocation than to the C:N ratio of each tissue, because allocation affects both the overall C:N ratio and storage lifetime. Changes in C:N ratios in response to N availability will never be as large as the difference between wood and foliage C:N ratios.

Gifford, Lutze & Barrett (1996) explored the assumptions about the partitioning of N deposition between different ecosystem pools using CQUESTN, a simple, globally aggregated model based on C and N pool sizes, turnover times, and nutrient ratios obtained from the literature. Nitrogen deposition was in the form of wet inorganic, wet organic, and dry deposition. The pre-industrial value was set to 20 Tg yr^{-1}, and the current value was assumed to be three times that. In different simulations the N was added directly into the next year's phytomass or entirely into soil organic matter (SOM), where it was then mineralized; 16% of the N was lost by volatilization and leaching. If the N input was directly into the vegetation, productivity and litterfall increased because photosynthesis in the model was stimulated by N. The effect on C sequestration was about 1.2 Pg in 1995. However, if the N deposition was put into the mineralizable SOM pool first, the effect on C sequestration was less than 0.2 Pg yr^{-1}. Reality is probably in between these extremes. Most N deposition enters an ecosystem through the soil, although some gaseous N compounds may be absorbed directly by foliage (Hanson *et al.*, 1989; Norby, Weerasuriya & Hanson, 1989). The N that enters the soil is competed for by roots and microbes, and the outcome of this competition will vary depending on how the N is added and the initial conditions of the plants and microbial populations (Aber *et al.*, 1989; Johnson, 1992). Gifford *et*

al. (1996) concluded that the assumption about how the exogenous N is initially taken up is a critical one that should be further investigated.

Hudson, Gherini & Goldstein (1994) employed a very different approach to the calculation of N-stimulated C storage. The historical record of atmospheric CO_2 concentration was deconvoluted using the historical record of fossil fuel emission and the ocean submodel of their global carbon cycle model (GLOCO) for the period 1850 to 1985. The remaining C flux was assumed to represent the perturbation of the terrestrial biosphere, including both net emissions from land use change and uptake from fertilization. Using GLOCO's terrestrial submodel to account for land use change, Hudson *et al.* (1994) inferred that significant fertilization must have occurred. The modeled response to historical increases in CO_2 and temperature accounted for 31% of the fertilization, and this implied that N fertilization must account for the rest. An anthropogenic N deposition rate of 1.1 g N m^{-2} yr^{-1} for 1980 in the temperate forest biome gave good agreement with the deconvolution record. This flux corresponds to 30 Tg N yr^{-1} in recent years and effects an increased C storage of about 1.3 Pg C yr^{-1}, or 70 Pg C from 1850 to 1985.

Implications and uncertainties

These various efforts to estimate the global C sink that can be attributed to anthropogenic N have yielded a relatively narrow range of response despite the large number of uncertainties. The global carbon budget of the 1995 IPCC assessment (Schimel *et al.*, 1996) assumes that N fertilization accounts for 1 Pg C yr^{-1}. The different approaches to the question have been valuable in highlighting some of the critical uncertainties. The most important of these is the uncertainty in the amount and distribution of different forms of N deposition—the basic input from which all of the calculations must start. But uncertainties in ecosystem processes also are important, including N retention as a function

of ecosystem type and N loading, initial distribution of N deposition between plant and soil pools, the C:N ratio of different ecosystem pools, and the flexibility of allocation patterns as a function of N input.

The issue of ecosystem retention of N may be of particular relevance to global change questions. Nitrogen saturation has been observed in forests subjected to high rates of N deposition (Waring, 1987; Aber *et al.*, 1989), leading to the concept of a critical load of N to an ecosystem (Schultze *et al.*, 1989). As implemented in the model of Townsend *et al.* (1996), the positive effect of N deposition on C sequestration declines as an ecosystem approaches N saturation and N retention decreases to zero. Nitrogen saturation is usually thought to be controlled primarily by the uptake of available N by vegetation (Schultze *et al.*, 1989; Aber *et al.*, 1989), so as a forest stand ages and its annual N increment begins to decline, leaching losses of nitrate begin to increase (Johnson, 1992). But soil can also accumulate N—litter and soils were the major sinks for N in many forest fertilization studies (Johnson, 1992). There was 100% retention of N fertilizer added periodically to two forests over three years (Aber *et al.*, 1993). Since the added N could not be found in vegetation components, it was assumed to have been transferred to SOM.

Can fertilization experiments provide a reasonable surrogate for atmospheric deposition of N? The competition between plants and nitrifying bacteria is of paramount importance. Small, frequent additions of N to an N-deficient system will cause more leaching than is observed in a traditional fertilizer application because the population of nitrifiers is stimulated. However, in an N-rich system with a large population of nitrifiers, leaching is more likely to be proportional to the amount rather than the frequency of input (Johnson, 1992). A substantial proportion of N deposition to a forest, however, is dry deposition, which can be absorbed directly by the canopy (Lindberg *et al.*, 1986). In contrast with fertilizer additions directly to the soil, there is no apparent relationship between ecosystem retention of atmospherically deposited N and the amount of input. The N increment in vegetation

accounts for most of the retention, with very low retention by the soil (Johnson, 1992). Ecosystem retention of N deposition is a critical factor in the calculation of the relationship between C storage and N deposition, as well as a determinant of many of the potentially deleterious effects of N deposition (Vitousek *et al.*, 1997). Current modeling approaches do not distinguish between canopy uptake of dry deposition and additions of N directly to the soil pools, and they must necessarily make simplifying assumptions about the retention of the deposited N. Clearly these are issues that needs greater understanding.

These analyses have shown that some of the C that is released to the atmosphere during fossil fuel combustion is removed from circulation because of the co-emission of reactive N. As the capacity of ecosystems to absorb additional N declines, the concurrent absorption of CO_2 will decline as well. Hence, a larger fraction of CO_2 will remain in the atmosphere where it can alter the earth's radiation balance, and the excess N can leach into streams and drinking water and cause environmental degradation (Vitousek *et al.*, 1997). Certainly, the apparently positive effect of N deposition in creating a sink for excess atmospheric CO_2 is not something we can be sanguine about.

CO_2 FERTILIZATION AND N LIMITATION

Experimental evidence

In some of the models discussed above the increase in CO_2 concentration from its pre-industrial value of 280 ppm to its current level of 360 ppm was one of the factors influencing C sequestration. Most research efforts on the effects of CO_2 concentration on plant productivity and C sequestration, however, are focused toward the increases in atmospheric [CO_2] that will occur over the next century. But whether we are looking back toward 1845 or forward to 2045, ecosystem response to CO_2 and N must be considered together.

Researchers on the effects of elevated CO_2 on plants have long recognized the important modifying influence of nitrogen nutrition. Kramer (1981) questioned whether forests that are currently limited in their growth by lack of sufficient available nitrogen could respond to increasing CO_2 concentrations. At that time, most of the research on plant responses to CO_2 centered on agronomic or horticultural crops that were well fertilized. Subsequent research with tree seedlings and components of other natural ecosystems that are usually not fertilized often focused on $CO_2 \times N$ interactions. Some studies have indicated that CO_2 responses are nullified or greatly muted when N is deficient (Bazzaz, 1990). Johnson & Ball (1996) concluded that a CO_2 response in *Pinus ponderosa* was prevented only under the most severe N limitation. Generally, we have concluded that N deficiency does not necessarily preclude growth responses to high CO_2 (Norby, O'Neill & Wullschleger, 1995). The mean response of many controlled studies with tree species indicates that the stimulation of growth by high CO_2 was reduced only slightly (from 36% to 28%) when plants were grown in what was thought to be N-deficient soil (Wullschleger, Norby & Gunderson, 1997).

To be useful for addressing longer-term responses of ecosystems to high CO_2, controlled experiments must identify the mechanisms of response to CO_2 and their interaction with N. Seedling studies suggested that plants might be able to acquire more N from soil through increased root exploration, mycorrhization, or root activity (Norby *et al.*, 1995). Mature trees in a forest rely primarily on recycling for most of their N requirement. Younger trees used in experimental studies, however, have no nutrient cycle (Johnson & Ball, 1996). Their N requirement is met primarily by expanding the root system into unexploited soil, a mechanism that is precluded in a closed forest stand that has fully occupied the soil. Although studies of young, isolated plants can identify physiological mechanisms of response, they cannot directly address the potential nutritional constraints that will temper long-term responses to elevated CO_2 (Johnson & Ball, 1996).

A common response in many seedling studies has been that N concentration is lower in plants grown in high CO_2 (McGuire, Melillo & Joyce, 1995). This is often interpreted as an increase in nutrient-use efficiency, possibly related to leaf-level biochemical adjustments (Ceulemans & Mousseau, 1994). Extending these results to the ecosystem level has proven difficult, especially for forest ecosystems. Increased N-use efficiency cannot be sustained indefinitely on a fixed capital of N; unless N availability increases, the response to high CO_2 will decline with time (Norby *et al.*, 1986). Field studies suggested that N mineralization might be stimulated in CO_2-enriched systems (Zak *et al.*, 1993), but this response apparently only occurs in systems with very low SOM content (D. R. Zak, personal communication). With these considerations in mind, increased input of N into an ecosystem may be particularly important for sustaining a response to elevated CO_2.

There are few experimental results that directly pertain to the interaction between N deposition and CO_2. Most $CO_2 \times N$ studies have used a single pulse application of fertilizer, which is probably a poor analogy for a persistent low level of N input characteristic of atmospheric deposition. Additions of fertilizer to a pot are especially problematic because the total N capital available to the confined plant can change drastically during the course of the experiment (Norby & O'Neill, 1991). A few early greenhouse studies inadvertently fumigated plants with a combination of CO_2 and NO_x because the CO_2 was generated by propane or kerosene heaters that also generated NO_x (Capron & Mansfield, 1977; Mortensen, 1985). Foliar uptake of the NO_x generally led to phytotoxic effects (Wellburn, 1990), but the NO_x concentrations in this situation exceeded those in rural landscapes by two orders of magnitude (Lindberg *et al.*, 1986), and the results are probably not relevant to global change analyses. Hättenschwiler, Schweingruber & Körner (1996) found that elevated CO_2 and N fertilization designed to mimic N deposition had opposite effects on wood density of *Picea abies*: wood density was increased by CO_2 fertilization but decreased by N deposition. Perez-Soba *et al.* (1994) investigated

interactions of NH_3 and CO_2 in *Pinus sylvestris* saplings, but since most global change analyses focus on NO_y deposition, the results are difficult to incorporate into the current analysis. The role of NH_x in global change is a topic that will need further attention.

Predictions from ecosystem models

With a general absence of empirical evidence, we must again rely on models of ecosystem response to CO_2 to evaluate the potential role of N deposition in the future. Those models should be evaluated in the context of other observations of N influences on the responses to CO_2 enrichment. Whether or not a model was specifically designed to investigate the role of N deposition, it must include some considerations of C-N interactions to be at all realistic. Rastetter *et al.* (1992) suggest that the three key biogeochemical processes for explaining C storage are: (1) the relative importance of external *vs.* internally recycled sources of N and other elements; (2) the distribution of C, N, and other elements between vegetation and soil; and (3) the flexibility of element ratios in vegetation and soil. An ecosystem with an external supply of N can increase C storage without a change in stoichiometry; otherwise there must be a redistribution from components with low C:N ratios (SOM) to components with high C:N ratios (woody biomass), or the C:N ratio of the components must increase. The more open a system is to external sources *vs.* internal cycling, the more responsive its C storage capacity to CO_2 should be (Rastetter *et al.*, 1992). Models to predict the CO_2 response of N-limited ecosystems must make some assumptions (explicitly or implicitly) about points 2 and 3 above. A critical question with regard to N deposition is the extent to which the increase in external N cycling (point 1) relieves the constraints implied by points 2 and 3.

Thornley & Cannell (1996) evaluated the combined effects of CO_2 and N deposition for a managed conifer plantation in upland Britain. They used the ITE Edinburgh Forest Model, which

describes changes in pools and fluxes of C, N, and water in a coupled forest-soil system parameterized for a 350, 550, 750 ppm CO_2, 20 or 40 kg ha^{-1} yr^{-1} N input (20 kg ha^{-1} yr^{-1} is the current ambient N deposition for the site), and three annual temperatures. The various combinations led to a wide variety of results traceable to the interacting effects on the C, N, and water dynamics of the system. The crucial processes were those affecting the N cycle, including C and N allocation, N uptake dependence on root mass and C:N ratio, N retranslocation dependence on internal C:N ratios, soil C and N dynamics and leaching.

The simulations suggested that CO_2 could increase productivity even in N-limiting conditions owing to increased N acquisition and use efficiency. In N-limiting conditions CO_2 increased allocation to roots with little increase in LAI, whereas in N-rich conditions high CO_2 increased LAI. Doubling N inputs increased NPP less than increasing CO_2 from 350 to 550 ppm. Carbon sequestration increased 56% at 750 ppm at low N and 91% in N-rich conditions. These increases, which are larger than those generally observed experimentally (Ceulemans & Mousseau, 1994; Wullschleger *et al.*, 1997), were associated with exceptionally large increases in the maximum rate of photosynthesis. The total amount of N in trees, harvested products, litter, and soil increased 28% at ambient N and 69% in N-rich conditions. This was traced to a reduction in leaching losses at high CO_2 due to more roots and lower soil solution N concentrations. There was a positive litter quality feedback: poorer litter quality at high CO_2 meant slower decomposition, lower soil NO_3^- concentration, and less leaching loss. Volatilization losses of NH_4^+ also were reduced by CO_2 (offsetting the effects of high temperature) because the NH_4^+ pool size was smaller. There was little effect of CO_2 on nitrification and denitrification because smaller pool sizes were offset by greater microbial populations (Thornley & Cannell, 1996).

Medlyn & Dewar's (1996) model of forest productivity responses to CO_2 enrichment and N deposition is highly dependent on assumptions about C allocation. Their essential assumption was that

plant growth responses to N deposition occur through increased light absorption and not through an increase in light use efficiency (ε). NPP increased with N deposition because LAI increased. The effect of high CO_2 on NPP was through increased ε, but this response was moderated by compensatory adjustments in LAI as imposed by constraints in the N supply. The net effect of CO_2 and N deposition depended on assumptions about allocation between sapwood, foliage, and fine roots. If the proportion of NPP allocated to sapwood was fixed, then NPP was completely constrained by the N cycle, since the amount of N sequestered into slow pools (heartwood and SOM) at equilibrium matched N inputs. Higher photosynthesis rates in high CO_2 (increased ε) were offset by lower LAI, and there was no increase in NPP or wood production. On the other hand, if allocation to sapwood was coupled to allocation to foliage, then more N was sequestered in wood and less in SOM. Increased CO_2 led to higher NPP and lower LAI, but sapwood respiration was increased such that wood production was lower than in the fixed-allocation case. With N deposition increasing N inputs, NPP increased regardless of assumptions about allocation, but with the multiple element limitation implied by foliage-sapwood coupling, N deposition allowed a greater response to increased CO_2.

This modeling approach illustrates that the responses to N deposition and CO_2 enrichment are not likely to be simple or additive. This is not surprising given the close linkages and feedbacks between the C and N cycles in a plant. The importance of the different assumptions about allocation on the net effect of N deposition and CO_2 enrichment clearly define several important research topics. Current research on CO_2 responses of trees has led to some similar assumptions about long term responses. A compensatory downward adjustment in leaf area was observed in *Liriodendron tulipifera* saplings in response to CO_2 enrichment, and this was interpreted in terms of an allocation adjustment between leaves and fine roots (Norby *et al.*, 1992). The relative constancy of the response of annual stem production per unit leaf area to high CO_2 was noted in field-grown broadleaf trees

despite differences in soil fertility and other aspects of experimental protocol (Norby, 1996). A hypothesis for longer term responses based on this observation is that leaf function (net photosynthesis or ε) will be stimulated by high CO_2 regardless of other environmental factors, but the overall growth (or NPP) response would be moderated by factors such as N supply that alter LAI. The difficulty in growing trees in controlled CO_2 concentrations to canopy closure and beyond has prevented any direct tests of this concept, but a new generation of free-air CO_2 enrichment experiments in closed-canopy forest stands should provide a test of the hypothesis.

More experimental results and observations exist to evaluate the assumptions about canopy responses to N. Does increased N result in higher rates of photosynthesis or in increased LAI? Vose & Allen (1988) reported that N fertilization of *Pinus taeda* trees increased LAI and foliar N concentration on N deficient stands, but wood production per unit leaf area was not affected. Lennon *et al.* (1985), however, showed that there was no difference in leaf production in *Acer saccharum* across a steep gradient of N mineralization. They concluded that LAI, canopy N, and production are related to soil N availability only when availability is low. Tschaplinski & Norby (1991) provided different amounts of N fertilizer to *Platanus occidentalis* trees. Fertilization did not alter foliar N concentration, but increased LAI, and the higher LAI contributed to faster growth early in the growing season. Photosynthesis increased in the latter part of the growing season and contributed to growth increases. Differences in whether LAI or photosynthesis is enhanced by N inputs could be related to prevailing growing conditions: if water is available, LAI is stimulated; otherwise photosynthesis is stimulated (Tschaplinski & Norby, 1991).

The MBL-GEM model (Rastetter *et al.*, 1992) is structured around C-N interactions and the transfer of N between pools with different C:N ratios. If N is mineralized from SOM (low C:N ratio) and incorporated into vegetation (high C:N ratio), then C storage increases without requiring any more

N. But if disturbance leads to transfer of N from vegetation to SOM, then C is lost. The bigger the difference in C:N ratio between vegetation and soil, the more important the control on N distribution in determining C storage response. The flexibility of ratios determines how closely linked the cycles are to one another. If the C:N ratio in vegetation is flexible such that N concentration can decrease in response to lower N availability, then C cycling through vegetation is less severely constrained by the N cycle and the ecosystem can respond more to increased CO_2.

The MBL-GEM model was used to simulate the response of a tundra and forest to twice ambient CO_2 (Rastetter *et al.*, 1992). In both forest and tundra, C storage increased because the C:N ratio of vegetation and soil increased. Since litter also had a high C:N ratio, soil N was immobilized, reducing N availability and amplifying the decline in the vegetation C:N ratio. N inputs in these simulations were low (1 g m^{-2} yr^{-1} for the forest and 0.06 g m^{-2} yr^{-1} for the tundra) and contributed very little to C storage. These inputs were then increased by ten-fold, and outputs were increased as well so there was no net N accumulation. This increased flux through the inorganic N pool buffered transient changes in inorganic N concentration. When elevated CO_2 was combined with increased N inputs, C storage increased about 20% in the tundra and 40% in the forest. There was a shift of N from soil to vegetation—the opposite of what occurred with lower N inputs. Although there were transient changes in C:N ratio, the net effect on C storage was due to the shift from soil to vegetation.

The MBL-GEM model ran on an annual time step and included very little plant physiology. McGuire *et al.* (1997) point out that N limitation does not completely constrain the response of NPP to increased CO_2 because of seasonality in the degree of N limitation, an issue that may be particularly important in regard to the patterns of N deposition. The TEM model (McGuire *et al.*, 1997) emphasizes the importance of N cycling within the plant and between plant and soil. Based on results of CO_2 manipulation and N fertilization experiments, they concluded that the ecosystem-level response

of carbon assimilation to elevated CO_2 may depend on how N uptake by the vegetation and N recycling within the vegetation influence the ability of plants to incorporate elevated CO_2 in the construction of canopy, stem, and root biomass. In TEM, N is allocated to represent the tradeoff between canopy development and acclimation of tissue-level photosynthesis so that C uptake is maximized in building vegetative biomass at a specific C:N ratio. That C:N ratio is not constant, however, because of seasonal changes in resorption and mobilization of N.

Gifford *et al.* (1996), using CQUESTN, emphasized that, because of compensations between C and N cycles, different model assumptions can lead to similar net results. For example, if a CO_2 stimulation of N mineralization was included (cf. Zak *et al.*, 1993), a large increase in vegetation C could offset a decrease in SOM. This potential interaction between CO_2 and N also illustrates the importance of the larger question: does the C cycle constrain the N cycle or *vice versa*? Gifford *et al.* (1996) concluded that N supply controls C cycling on seasonal time scale, but C controls N acquisition by an ecosystem over the long term. It is a perspective that seems particularly relevant to the role of N deposition in the future.

Other issues

The inferences from these ecosystem models generally support the conclusion that elevated CO_2 will lead to higher NPP and C sequestration even when N is limiting. Hence, N deposition is not *necessary* for there to be a CO_2 fertilization effect. Nevertheless, the response of ecosystems to CO_2 would be expected to be larger, and the range of possible responses wider, in ecosystems with increased N input because of deposition. However, there are a number of other issues that must be included in this analysis. As N deposition pushes a system closer to its N retention capacity, enough changes in the composition and dynamics of the ecosystem may result that equilibrium predictions are no longer

relevant.

Could the stimulation of plant growth processes by increased CO_2 forestall or accelerate the development of N saturation? This is not a topic that has been considered in detail, but some of the mechanisms of CO_2 response could potentially influence nitrate leaching. If there is greater sequestration of N in wood in elevated CO_2, relatively less should be available to be leached, as long as any atmospheric deposition that enters the soil nitrate pool is taken up fast enough. Carbon dioxide enrichment of *Pinus taeda* saplings increased the root uptake capacity for nitrate but not of ammonium (BassiriRad *et al.*, 1996). This response could allow for greater ecosystem retention of nitrate, thereby mitigating the detrimental effects of N deposition (BassiriRad *et al.*, 1996). Assimilation of gaseous forms of N deposition (e.g., NO_2 and HNO_3 vapor) requires the presence of the enzyme nitrate reductase. Carbon dioxide enrichment reduced the level of nitrate reductase activity in *Alnus serrulata* seedlings (Norby *et al.*, 1984). However, it is unlikely that this response would really lead to reduced rates of foliar N assimilation. Even *Picea rubens* seedlings, which would normally be expected to assimilate very little nitrate in their needles, had sufficient constitutive levels of nitrate reductase to assimilate the amount of HNO_3 vapor or NO_2 that occurs in forests (Norby *et al.*, 1989). There has been some speculation that CO_2 enrichment adds enough labile C to the soil to stimulate microbial activity (Zak *et al.* 1993; Körner & Arnone, 1992), which could lead to increased nitrification rates and increased leaching if the system is already close to N saturation. However, there are so many positive and negative feedbacks on nitrification that this speculation seems untenable as a general conclusion.

Nitrogen saturated systems can be expected to undergo a more rapid species replacement than might otherwise be expected. Nitrogen availability can have significant negative effects on species richness and other aspects of the structure and dynamics of plant communities (Tilman, 1987; Goulding *et al.*, 1998). If N deposition leads to changing species composition, then all of the responses to

elevated CO_2 or N deposition that depend on allocation to components with different C:N ratios will change. The response of mixed communities to CO_2 can differ considerably from those of individual species (Bazzaz, 1990). Although models are now beginning to deal with species replacement and biogeography along with direct effects of CO_2 (VEMAP members, 1995), it is difficult enough to predict the responses of a static system. Nevertheless, it is important to remember the diversity of responses that might occur when this added complexity is considered. It also must be remembered that climate change is predicted to accompany the increase in CO_2 and N deposition. Microbial decomposition of SOM is strongly temperature dependent; increased mineralization is an expected response to climatic warming, further altering N dynamics (Davidson, 1995).

VOLATILIZATION AND TRACE GAS INTERACTIONS

Nitrous oxide

A pre-industrial ecosystem would be expected to be in balance with respect to N; that is, any input of N into the system (from biological N_2 fixation or fixation by lightning) would be matched by losses of N from the system. The most important mechanism of N loss in undisturbed systems is volatilization through denitrification. Denitrification is the microbially-mediated conversion of NO_3^- to N_2 or N_2O. In addition, nitrification can produce N_2O as a byproduct, and NH_4^+ can deprotonate in alkaline soils leading to volatilization of NH_3 (Bowden, 1986). Denitrification requires low oxygen conditions (but not necessarily anaerobic soils) and a supply of nitrate and reduced carbon. The potential for N volatilization from natural ecosystems is only realized under certain environmental conditions.

Losses of N (primarily as leaching losses) have already been considered in relation to N retention by ecosystems and the effectiveness of N inputs in stimulating C storage. Volatile emissions of N_2O have another more important link to global change issues. N_2O is a potent greenhouse gas.

Since it is very nonreactive (biologically or chemically) in the troposphere, it has a long residence time (120 years) and is only destroyed in the stratosphere in reaction with ozone (Schimel *et al.*, 1996). Stratospheric ozone destruction is associated with increased penetration of damaging uv-b radiation to the earth's surface. The radiative forcing of a single N_2O molecule is 200 times that of a CO_2 molecule, and overall it is one of the most important radiatively active gases besides CO_2 (Schimel *et al.*, 1996). The concentration of N_2O in the atmosphere has been increasing at 0.25% per year (compared to 0.4% for CO_2). All of the sources of this increase have not been determined. More than half of the total global N_2O emissions come from natural soils, and about 30% are attributable to fertilization, cultivation and biomass burning (Schlesinger, 1991). Although data are scant, there are many possible ways in which disturbance could accelerate N_2O emissions. Fertilization often leads to large increases in N_2O production (Field *et al.*, 1992); N deposition can be expected to stimulate N_2O efflux as well (Smith, 1997; Goulding *et al.*, 1998). Elevated CO_2 also could conceivably alter N_2O emissions by changing the system water balance, stimulating microbial activity, or altering N cycling. Arnone & Bohlen (1997) reported that N_2O emission from intact monoliths of a Swiss grassland were doubled after a two-year exposure to elevated CO_2.

Tropospheric ozone

Nitrogen oxides must be considered as trace gases in the atmosphere in addition to a form of N deposition to ecosystems. They are the most important precursors of tropospheric ozone (O_3) and photochemical smog (Schlesinger 1991; Chameides *et al.*, 1994). There have been a number of investigations of the interactions between O_3 and elevated CO_2 on trees, grasses, and agricultural plants (e.g., Volin & Reich, 1996; Mulholland *et al.*, 1997; Reinert, Eason & Barton, 1997). Since elevated CO_2 usually reduces stomatal conductance (Ceulemans & Mousseau, 1994), and lower conductance

reduces plant uptake of ozone and subsequent damage (Reich & Amundson, 1985), it is generally found that elevated CO_2 will provide some degree of protection against the phytotoxic effects of ozone. There are, however, exceptions to this general rule (Kull *et al.*, 1996). Most considerations of ozone effects concern the present and near-term effects. The annual increase of CO_2 (about 1.5 ppm) is too small to influence near-term ozone effects. If the tropospheric ozone concentration continues to increase in concert with increasing NO_y emissions (Chameides *et al.*, 1994), the $CO_2 \times O_3$ interaction could become an increasingly important issue.

CONCLUSIONS

The nitrogen cycle is probably the most complex of terrestrial nutrient cycles. That complexity is increased manyfold by the multiple points of intersection of the N cycle with the C cycle and the large-scale perturbations of both cycles through human activities. The analyses and discussion presented here reflect much of that complexity. There is no one way to model C-N interactions, whether in a single plant, a specific ecosystem, or the entire terrestrial biosphere. Even if there were, the geographic and chemical distribution of N deposition is not known well enough to support rigorous, quantitative predictions about the role of N deposition in carbon sequestration. The discussion here has largely ignored the complicating—but undoubtedly important—factors of climate change and species redistribution.

Despite all of the simplifying assumptions, some conclusions can be made. Deposition of reactive N compounds resulting from human activities, particularly nitrogen oxides derived from fossil fuel combustion, has most probably increased the amount of C taken up from the atmosphere and sequestered in terrestrial ecosystems. Additional anthropogenic sources of N, including NH_x, are probably also important in global C sequestration, but their role is less studied

and more uncertain. The continued occurrence of N deposition to some currently N-limited ecosystems will probably allow a greater CO_2 fertilization in the future. Both of these responses should slow the increase in atmospheric CO_2 concentration and, therefore, slow the development of climate change. At the same time, however, both N deposition and increasing CO_2 concentration might cause an increase in N_2O emissions from some ecosystems. As a potent greenhouse gas, an increased flux of N_2O would counteract any savings accrued from increased C sequestration. Besides, any increased C sequestration resulting from N deposition is a somewhat illusory benefit of the N inputs. The NO_y inputs originate from the fossil fuel combustion that also creates the CO_2 problem. The simultaneous sequestration of C and N simply returns to a nonreactive pool a portion of the elements that were released from that pool by combustion. There is no net gain associated with the N deposition, and there are many other detriments to human and environmental health. There is little doubt that N production will increase in the coming decades: anthropogenic N_2 fixation is driven by energy and food production, and therefore by population and standard of living (Galloway *et al.*, 1995). Nitrogen deposition must be an important part of global change analysis, and the challenges it presents to the management of our planet must be faced.

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